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الجامعة الأردنيــة
كلية الدراسات العليا

التاريـــخ: / /

نموذج رقم (١٨)
اقرار والتزام بقوانين الجامعة الأردنية وأنظمتها وتعليماتها لطلبة الماجستير

أنا الطالب: باسل مصطفى محمود حمز الرقم الجامعي: ٨٠٦١٧١٥
التخصص: الكيمياء الكلية: العلوم

اعلن بأنني قد التزمت بقوانين الجامعة الأردنية وأنظمتها وتعليماتها وقراراتها السارية المفعول المتعلقة باعداد رسائل الماجستير والدكتوراة عندما قمت شخصيا" باعداد رسالتي / اطروحتي بعنوان: ....
Modification of Jordanian clays by using prepared fatty hydroxamic acids (FHAs) from several vegetable oils
....

وذلك بما ينسجم مع الأمانة العلمية المتعارف عليها في كتابة الرسائل والأطاريح العلمية. كما أنني أعلن بأن رسالتي /اطروحتي هذه غير منقولة أو مستلة من رسائل أو أطاريح أو كتب أو أبحاث أو أي منشورات علمية تم نشرها أو تخزينها في أي وسيلة اعلامية، وتأسيسا" على ما تقدم فانني أتحمل المسؤولية بأنواعها كافة فيما لو تبين غير ذلك بما فيه حق مجلس العمداء في الجامعة الأردنية بالغاء قرار منحي الدرجة العلمية التي حصلت عليها وسحب شهادة التخرج مني بعد صدورها دون أن يكون لي أي حق في التظلم أو الاعتراض أو الطعن بأي صورة كانت في القرار الصادر عن مجلس العمداء بهذا الصدد.

توقيع الطالب: .... التاريخ: ٢٣ / ٨ / ٢٠١١

MODIFICATION OF JORDANIAN CLAYS BY USING PREPARED FATTY HYDROXAMIC ACIDS (FHAs) FROM SEVERAL VEGETABLE OILS

By
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This Thesis was Submitted in Partial Fulfillment of the Requirements for the Master's Degree of Science in Chemistry

Faculty of Graduate Studies
The University of Jordan

August, 2011

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COMMITTEE DECISION

This Thesis/Dissertation (Modification of Jordanian clay by using prepared fatty hydroxamic acids from several vegetable oils) was successfully defended and approved on 11/8/2011

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DEDICATION

TO MY FATHER, BROTHERS AND

SISTERS AND

SPECIALLY TO THE SOUL OF MY

MOTHER

Acknowledgment

First of all, this work would not be succeeded without the care of Allah; Allah provides me with strength and patience to complete this work and Allah deserve thanks in all cases.

I would like to express my deepest appreciation to Dr Imad Hamadneh and Prof. Fawwaz Khalili for their guidance and consultations during the research period. Both showed patience and provided fruitful suggestions enhancing the scientific value of my thesis.

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My deepest gratitude to my family for their love, support and efforts that contributed towards the completion of this dissertation. My family encouraged me to remain steadfast in my studies and to remain positive when times were difficult and for this I am indebted to them for the rest of my life. I promise my family that I will be the son and brother that will continue to make them proud by continuing to fulfill our dreams.

And above all else I would like to dedicate my dissertation to my mother who recently passed away. Her love and support will never fade. I love you mom.

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List of Abbreviations

Ben: Bentonite.

FA: Fatty Acid

FHA: Fatty Hydroxamic Acid.

FHS: Fatty Hydroxamic Salt.

FT-IR: Fourier Transform Infrared.

HRMS: High Resolution Mass Spectrometry.

ICDD: International Centre for Diffraction Data.

K: Kaolin.

KHP: Potassium Hydrogen Phthalate.

L.O.I: Loss of Ignition.

M.m: Molecular mass.

RK: Red Kaolin.

SEM: Scanning Electron Microscope.

UV-VIS: Ultra Violet – Visible.

WK: White Kaolin.

XRD: X-Ray Diffraction.

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ABSTRACT

This thesis concerns with the synthesis and characterization of fatty hydroxamic acid FHA from several vegetable oils namely, corn oil, palm oil, olive oil, soybean oil and sunflower oil. The synthesis of FHA from these vegetable oils was done by three methods, i) from fatty acids FA (carboxylic acid). ii) from methyl/ethyl fatty esters. iii) directly from triacylglyceride. The obtained FHA was characterized by colorimetric, FT-IR and mass spectroscopy. Three clays namely, white kaolin, red kaolin and bentonite were modified by these FHA. These modified clays were characterized by FT-IR, SEM and XRD. The results of all these techniques were verified the modification. The mass uptake experiments were done in acidic and basic media. The results showed that the mass uptake in acidic medium was higher than that in basic medium. The results revealed that the maximum mass uptake was obtained with palm FHA using red kaolin in acidic medium. Generally, the presence of long-chain (mainly 16 and 18 carbon atoms) in FHAs containing O and N atoms suggests that the FHAs should be very useful as surfactants for clay modification.

CHAPTER

ONE

INTRODUCTION

AND

LITERATURE

REVIEW

1.1 Introduction

1.1.1 Preface

Clay minerals constitute 16 % of the total material volume at the earth's surface. The term clay was initially defined as a consisting of grains less than 2 μm in diameter. As a rock, clay usually consists of mixture of minerals and other rocks debris of varying composition. Weathering of the silicate rocks provides clay as alteration products. During weathering reactions, a wide spectrum of clay minerals forms. The nature of the newly formed clay minerals depends not only on the chemistry of the parent rock but also on the reactive environment like climate, CO_2, waters, etc (Clifford and Gessuer, 1973).

The clay minerals are built up of tetrahedrally and octahedrally coordinated cations originated to form either sheets or chains. The basic structural units in the layer silicates are siloxane sheets $(Si_2O_5)^{2-}$ joined together with brucite or gibbsite sheets. The siloxane sheets are connected at three corners in the same horizontal plane forming a hexagonal network. The tips of the tetrahedra point in the same direction. The unit is called the tetrahedral layer. The brucite $[Mg_3(OH)_6]$ or gibbsite $[Al_2(OH)_6]$ sheet consists of two planes of hydroxy ions between which lies a plane of magnesium or aluminum ions, which is octahedrally coordinated by the hydroxyl groups. This unit is known as the octahedral layer. These layers are combined so that the oxygen at the tips of the tetrahedral layer project into a plane of hydroxyl groups in the octahedral layer and replace two-thirds of the hydroxyl groups (Brindley and Brown, 1984).

Jordan is rich in clays, which are important in various industries. The most two important and interest clays are Kaolin (K) and Bentonite (Ben) (Khoury, 2002).

1.1.2 Bentonite

Bentonite is a clay deposit consisting essentially of smectite minerals. Smectites are unique by their extreme small crystal size and variation in the internal chemical composition, and structural characteristics (Rauf and Tahir, 2000).

Smectites are classified depending on their crystalline and chemical composition as show in Table 1.1 (Al'ali, 1993).

Table 1.1. Crystalline structure and chemical composition for smectites.

Crystalline Structure	Chemical Composition
Dioctahedral	
Montmorillonite	$5Al_2O_3.2MgO.24SiO_2.6H_2O(Na_2O, CaO)$.
Beidellite	$13Al_2O_3. 5Fe_2O_3.38SiO_2.12H_2O(Na_2O, CaO)$.
Nontronite	$Al_2O_3. 6Fe_2O_3.22SiO_2.6H_2O(Na_2O, CaO)$.
Trioctahedral	
Hectorite	$16MgO.Li_2O.24SiO_2.6(Fe,H_2O) (Na_2O)$.
Saponite	$18MgO.Al_2O_3.22SiO_2.6H_2O (Na_2O,CaO)$.

Bentonite is a 2:1 type of clay, which means that it is composed of units of two silica tetrahedral sheets with a central alumina octahedral sheet. All tips of tetrahedron points in the same direction and toward the center unit, Figure 1.1 (Grim, 1968).

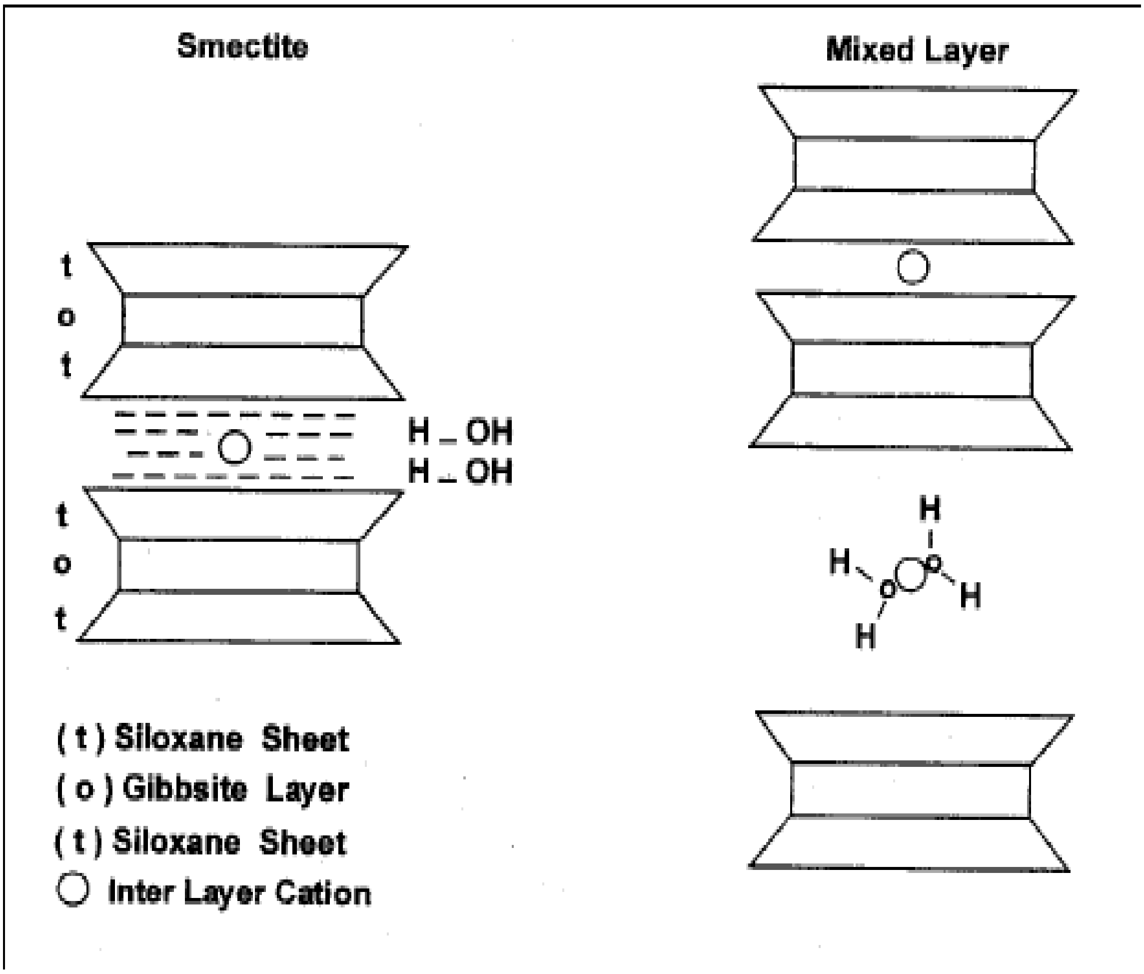


Figure 1.1. A sketch illustrating smectite and mixed layer structure (t = tetrahedral, o = octahedral) (Mitchell, 1993).

The tetrahedral sheets are siloxane $(Si_2O_5)^{2-}$ and the octahedral is gibbsite $[Al_2(OH)_6]$ or brucite $[Mg_3(OH)_6]$. The interlayer cations are present to balance the negatively charged structure that results from internal substitution of trivalent ions for silicion in the tetrahedral sheet and divalent ions for aluminium in the octahedral sheets. Interlayer surface and cation hydration between smectites structural units is a unique property of smectites, Figure 1.2 (Subramanian and Gupta, 2006). These layers are held together by weak Van der Waals forces, which ease the penetration of water molecules between the layers (Kaya and Oren, 2006).

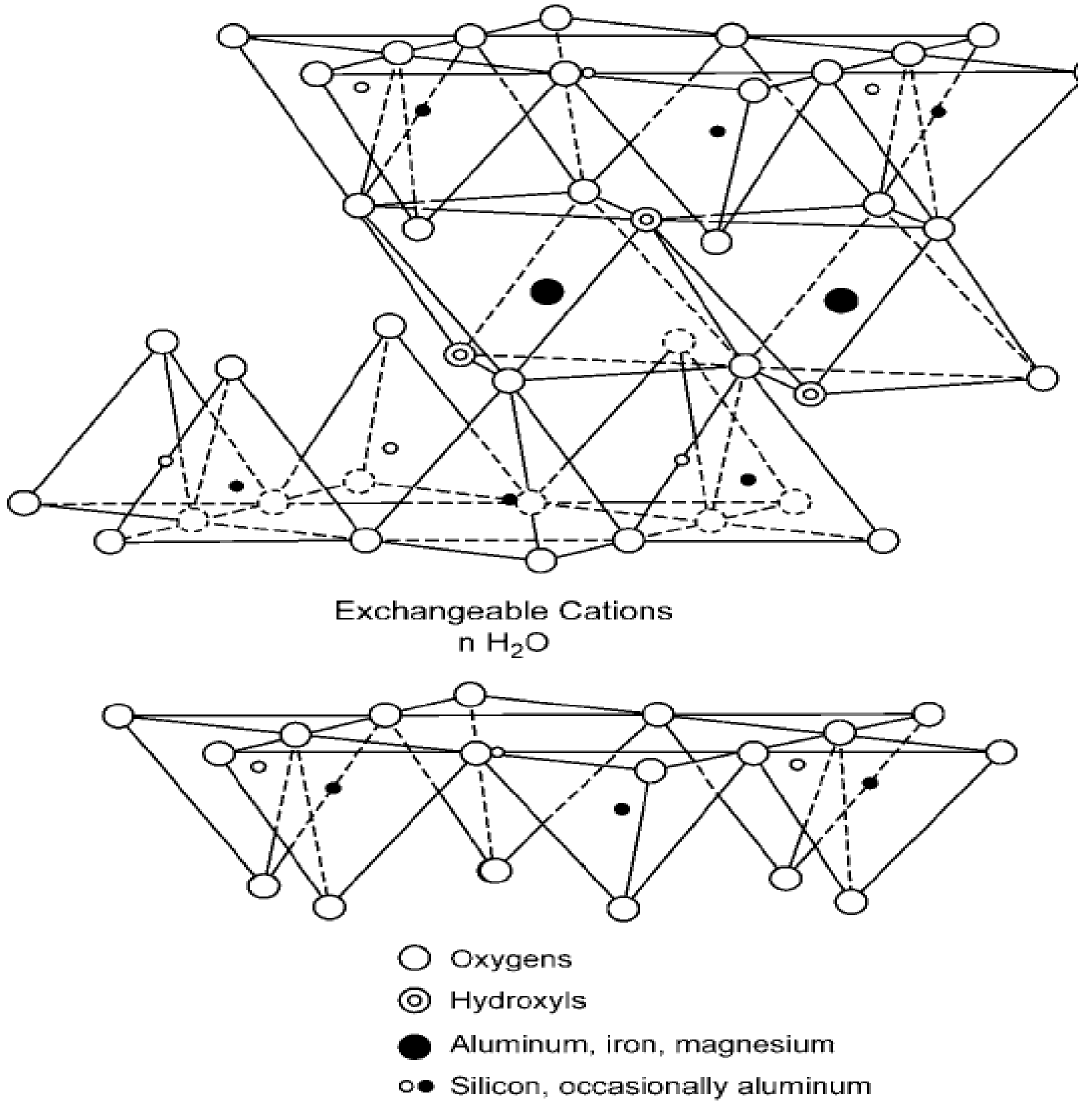


Figure 1.2. Diagrammatic sketch of the structure of smectite (Murray, 2007).

The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. This negative charge is balanced by the presence of exchangeable cations (e.g. H^+, Na^+ and Ca^{2+}) at the clay surface. Compared with other clay types, bentonite has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on the outer surface and edges (Yun, et al., 2006).

X-ray fluorescence studies showed that natural bentonite contains a complement exchangeable sodium, calcium and potassium cations. The (Na+K)/Ca ratio is 1.11. Low silica bentonite is enriched with calcium, whereas high silica bentonite is enriched with potassium, sodium and magnesium (Donat, et al., 2005).

The behavior of bentonite toward metal ions is governed with the dominant cation in its structure. In the case of bentonites dominated by sodium and calcium, the ions are quite mobile and hence when it is immersed in water, swelling occurs and metal exchange capacity is obtained. In the case of potassium bentonite, potassium ions are immobile and fit exactly into the interlamellar spaces created by the silicate structure and hence no swelling occurs when it is immersed in water; so potassium will suppress the metal ion adsorption (Donat, et al., 2005).

Bentonite has an enormous surface area when hydrated in water. It consists of numerous microscopic platelets, each with negative charge on the flat surfaces and positive charge on the edges. When hydrated, the water molecules cause these platelets to separate into a porous structure containing both negative and positive charge as shown in Figure 1.3 (Abu-Aitah, 2001).

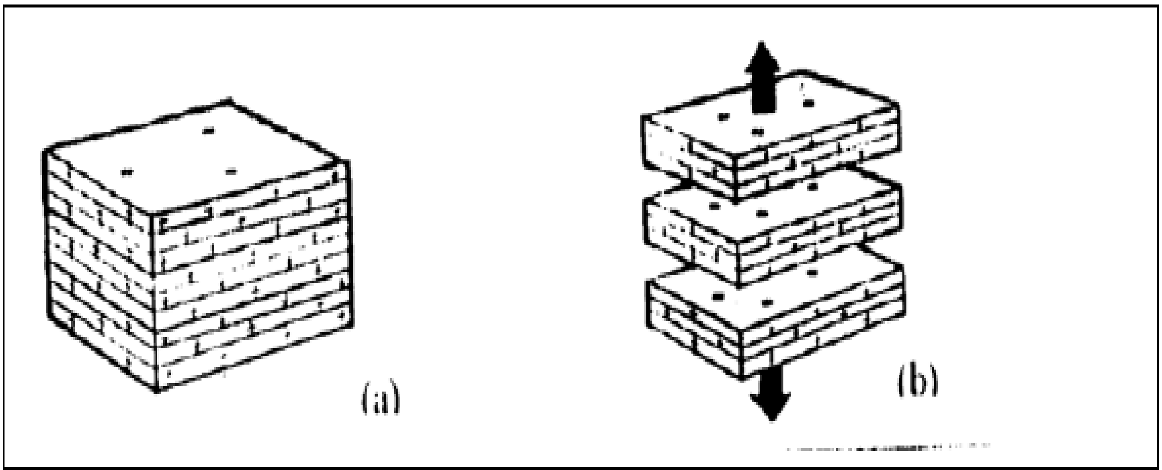


Figure 1.3. Effect of water on bentonite: (a) dry bentonite; (b) hydrated bentonite (Abu-Aitah, 2001).

1.1.3 Jordanian Bentonite

The main two areas containing bentonite deposits in Jordan are Al-Yamaniyya and Al-Azraq areas. Al-Azraq area is divided into two parts; Q'a Al-Azraq and Ein Al-Bayda areas while Al-Yamaniyya is located about 10 km south of Aqaba. Many researchers studied the physical and chemical properties of Al-Azraq bentonite, because of the important properties of Jordanian bentonite, it seized upon the interest of industrialists, environmentalist, agronomists, mineralogists and engineers. Some of these properties are listed in Tables 1.2 and 1.3 (National Resource Authority, 2006).

Table 1.2. Physical properties of Jordanian bentonite from Al-Azraq.

Property	Location	
	Q'a Al Azraq	Ein Al Bayda
Specific gravity g/cm^3	2.64-.72	2.49-.58
Specific surface area m^2/g	112.79- 468.34	370.30- 487.40
Smectite %	64.93	63.56
CEC Meq/100g	20.56-87.00	18.28-53.18
Oil absorption % (w/w)	60.70-87.20	70.0-74.0
Water absorption % % (w/w)	143.50-185.50	106.5-207.0
Attrition resistance %	80-95	80-83.5
Adsorption of water vapor %	11	17

Table 1.3. Chemical composition of Jordanian bentonite from Al-Azraq.

Oxides %	Location	
	Q'a Al Azraq	Ein Al Bayda
SiO_2	51.59	7.94-52.68
Al_2O_3	11.97	2.02-21.76
Fe_2O_3	2.09	0.97-9.14
MgO	5.88	1.06-12.80
CaO	4.17	0.63-4.28
Na_2O	3.42	0.01-4.99
K_2O	3.31	0.19-3.80
TiO_2	0.31	0.06-1.57

1.1.4 Kaolin

Kaolin is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra.(Murray, 1961).

Kaolin has a 1:1 layer structure, first suggested by Pauling (Pauling, 1930); with the basic unit consisting of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{3+} as the octahedral cation. The repeating layers of the mineral are hydrogen bonded together. (Trevino and Coles, 2003).

Both sheets combine to form a common layer such that the tips of the silica tetrahedral point towards the octahedral layer. The tetrahedral layer is inverted over the octahedral layer with the apical 'O' atoms being shared by the two layers; as shown in Figures 1.4 and 1.5 (Srivastava, et al., 2005).

The Al-atoms are placed in such a manner that any two Al-atoms are separated by two hydroxyl groups one above and one below; making a hexagonal distribution in a single plane in the centre of the octahedral sheet. The hydroxyl groups are placed directly against the centers of oxygen-hexagons of the basal plane of the tetrahedral layer. (Bhattacharyya and Gupta, 2008).

Kaolin, $(Si_4)^{IV}$ $(Al_4)^{III}O_{10}(OH)_8$, has the theoretical composition of SiO_2 46.54 %, Al_2O_3 39.50 %, H_2O 13.96 % expressed in terms of the oxides. The formula indicates that there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer and no substitution of Al^{3+} with other ions (e.g., Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Na^{+} or K^{+}) in the octahedral layer. Thus, the net layer charge of kaolin is: $[4 (+4)]+[4 (+3)]+[10 (-2)]+[8 (-1)]=0$, but in nature, kaolin has a small net negative charge arising from broken edges on the clay crystals. This negative charge, although small, is responsible for the surface not being completely inert; it allows electrostatic interaction with positively charged ions (Khoury, 2002).

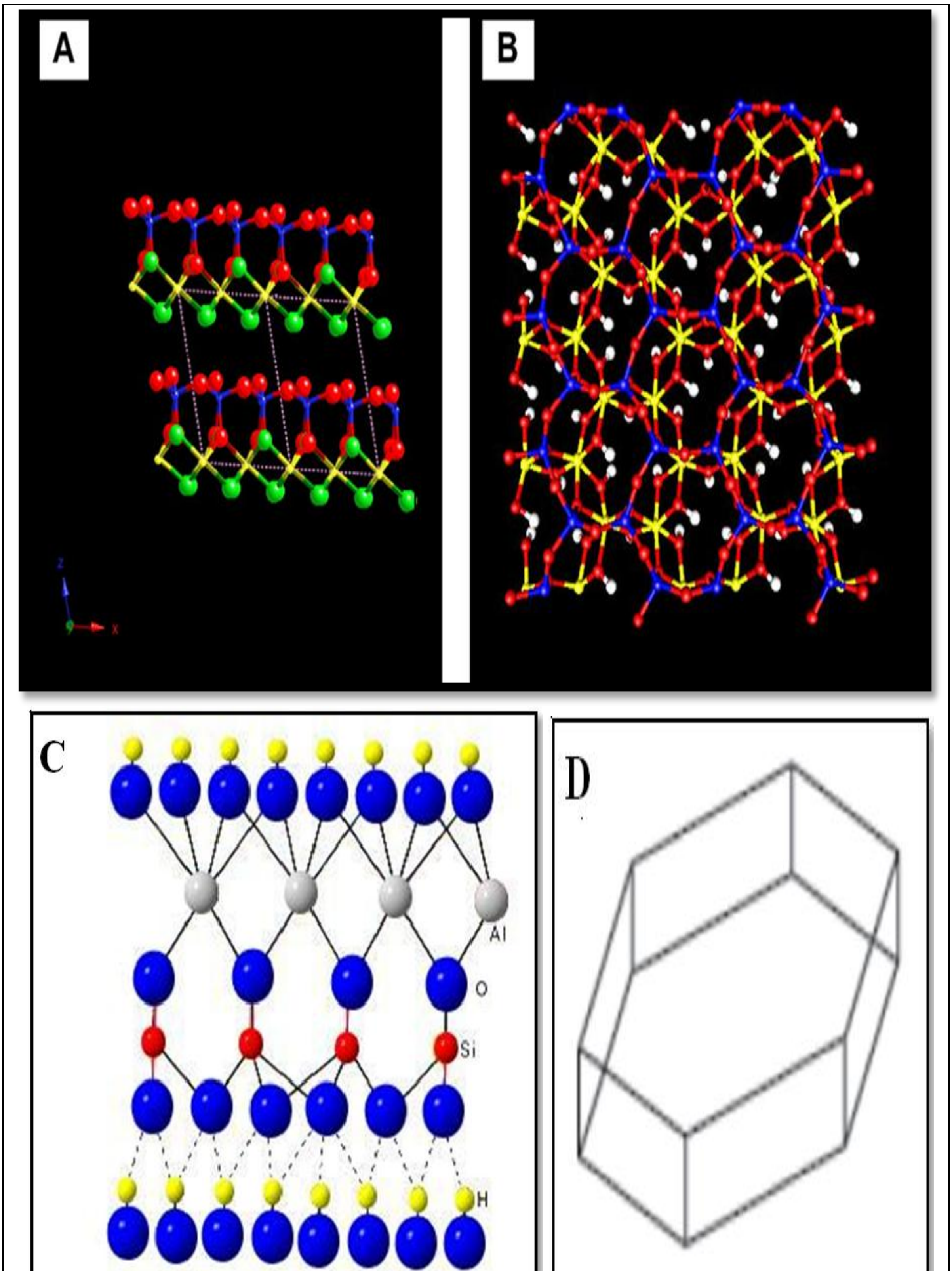


Figure 1.4. Surface structure of kaolin: (A) side view, (B) top view. the silica tetrahedral (red: oxygen, blue: silicon) and alumina octahedral (yellow: aluminum, green: hydroxyl) bilayers thought to be bound together via hydrogen bonding are illustrated in (A). (C) structure of kaolinite. (D) base shape of the kaolin crystal. (Gupta and Miller, 2010).

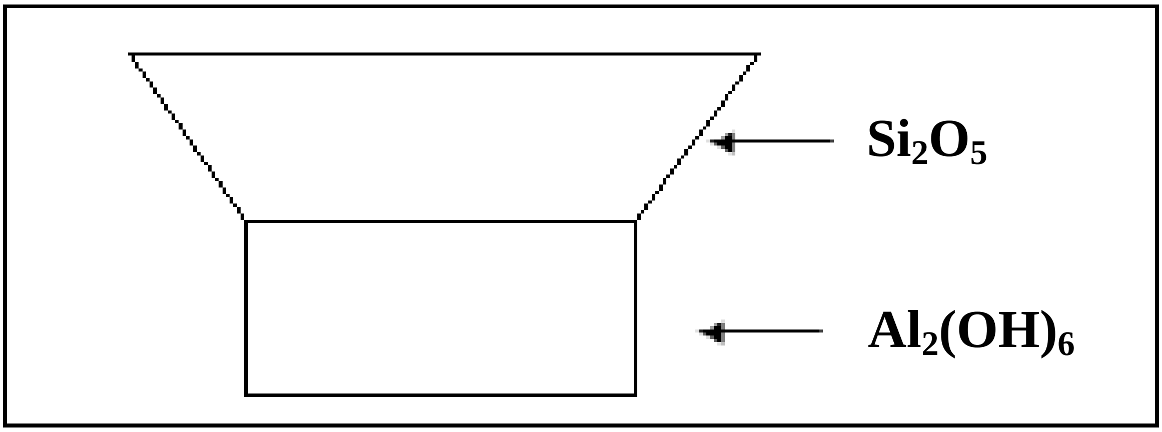


Figure 1.5. Schematic illustration of the crystal structural formulas of the kaolin with chemical formula $Al_2Si_2O_5$ $(OH)_4$ (Srivastava, et al., 2005).

Though kaolin is the least reactive clay, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment. A pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl (SOH) groups (Hizal and Apak, 2006, b), and they can become SOH_2^+ and SO^- at low and high pH, respectively (Angove, et al., 1997). The layer edges were exposed OH groups will exhibit acid–base behavior are primarily responsible for interaction of kaolin with environmental contaminant metals (Bhattacharyya and Gupta, 2008).

Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets. Cation adsorption mainly occurs on proton-bearing surface functional groups such as silanols and aluminols via covalent binding. (Hizal and Apak, 2006, b). The tetrahedral sheet of kaolin carries a small permanent negative charge due to isomorphous substitution of Si^{4+} by Al^{3+}. (Hizal and Apak, 2006, b) or of trivalent metal ions (such as Al^{3+}) by divalent ions (such as Fe^{2+} and Mg^{2+}) in the alumina octahedral sheet, leaving a single negative charge for each substitution. (Srivastava, et al., 2005).

1.1.5 Jordanian Kaolinite

The main four areas containing kaolinite deposits in Jordan are:

1- Mahis area: The kaolinite deposits in Mahis area (20 km north west of Amman) were investigated by Khoury, 1981.

2- Ghor-Kabid: Its clay deposits are located 2 km east of the Arda-Karama highway. The deposits were studied by Khoury and Ibrahim, 1986.

3- Hiswa: It is located 20 km to the southeast of Ad Disi village. The deposits were studied by Al-Momani, 2000.

4- Batn El Ghoul: Batn El Ghoul and Al Muddawwara clay deposits belong to Petra Mudstone Member of the Muddawwara Middle Sandstone Formation. Batn El Ghoul clays are located 65 km south-southeast of Ma'an in the southern part of Jordan, and it covers a surface of about 875 km^2. The deposits were studied in details by Khoury and El Sakka, 1986.

The chemical composition of Batn el Ghoul clay deposits are listed in Table 1.4 (National Resource Authority, 2006).

Table 1.4. Chemical composition of Batn El Ghoul clay deposits.

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	L.O.I
47.62	24.89	0.72	6.11	1.01	0.49	0.84	2.35	15.68

1.1.6 Fatty Hydroxamic Acids (FHA)

Hydroxamic acid (HA) or (*N*-hydroxycarboxylic amides), have the general chemical formula R-CO-NHOH. It is regarded to derivatives of both hydroxylamine and carboxylic acids (Miller, et al., 2002).

The term FHA came when (HA) prepared from fatty acids. A Fatty acid (FA) is a carboxylic acid with a long unbranched aliphatic chain, which is either saturated or unsaturated. FAs are usually derived from triglycerides. When they are not attached to other molecules, they are known as free fatty acids (FFA). The FA can be defined by its source (animals or plants), or by its carbon number as a short chain (fewer than six), medium (6-12), long (longer than 12), or very long (longer than 22), (Campbell and Farrell, 2006).

Even though, the FA can be defined also according to the number of double bonds as saturated (without double bonds), and unsaturated (one double bond known as monounsaturated, more than one double bond known as polyunsaturated), (Campbell and Farrell, 2006).

Tables 1.5 to 1.12 give examples of saturated FA, unsaturated FA, fats in some vegetable oils, fats in corn oil, fats in palm oil, fats in olive oil, fats in soybean oil and fats in sunflower oil, respectively.

Table 1.5. Examples of saturated FA (IUPAC, 1997)

Common name	Chemical structure	C:D *
Lauric acid	$CH_3(CH_2)_{10}COOH$	12:0
Myristic acid	$CH_3(CH_2)_{12}COOH$	14:0
Palmitic acid	$CH_3(CH_2)_{14}COOH$	16:0
Stearic acid	$CH_3(CH_2)_{16}COOH$	18:0
Arachidic acid	$CH_3(CH_2)_{18}COOH$	20:0
Behenic acid	$CH_3(CH_2)_{20}COOH$	22:0
Lignoceric acid	$CH_3(CH_2)_{22}COOH$	24:0
Cerotic acid	$CH_3(CH_2)_{24}COOH$	26:0

*C = carbon number; D = double bond number.

Table 1.6 Examples of unsaturated FA (IUPAC, 1997)

Common name	Chemical structure	C:D*
Myristoleic acid	$CH_3(CH_2)_3CH{=}CH(CH_2)_7COOH$	14:1
Palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	16:1
Sapienic acid	$CH_3(CH_2)_8CH{=}CH(CH_2)_4COOH$	16:1
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (cis)	18:1
Elaidic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (trans)	18:1
Vaccenic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$	18:1
Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	18:2
Linoelaidic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	18:2
α-Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	18:3
Arachidonic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$[NIST]	20:4
Eicosapentaenoic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	20:5
Erucic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	22:1
Docosahexaenoic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_2COOH$	22:6

*C = carbon number; D = double bond number.

Table 1.7. Fats in some vegetable oils (Food Standards Agency, 1991)

Vegetable oils	Saturated g/100g	Monounsaturated g/100g	Polyunsaturated g/100g	Cholesterol mg/100g	Vitamin E mg/100g
Palm	45.3	41.6	8.3	0	33.12
Soybean	14.5	23.2	56.5	0	16.29
Olive	14.0	69.7	11.2	0	5.10
Corn	12.7	24.7	57.8	0	17.24
Sunflower	11.9	20.2	63.0	0	49.0

Table 1.8. Fats in corn oil (U.S. Department of Agriculture, Agricultural Research Service. 2007)

Saturated fats	Palmitic acid 80 % Stearic acid 14 % Arachidic acid 3 %
Monounsaturated fats	Oleic acid 99 %
Polyunsaturated fats	Omega-6 linoleic acid 98 % Omega-3 alpha-linolenic acid 2 %

Table 1.9. Fats in palm oil (UK Food Labelling Regulations 1984)

Saturated fats	Laurate 0.1 % Myristate 1 % Palmitate 44 % Stearate 5 %
Monounsaturated fats	Oleate 39 %
Polyunsaturated fats	Linoleate 10 % Linolenate 0.3 %

Table 1.10. Fats in olive oil (UK Food Labelling Regulations 1984)

Saturated fats	Palmitic acid: 7.5–20.0 % Stearic acid: 0.5–5.0 % Arachidic acid: <0.6 % Behenic acid: <0.3 % Myristic acid: <0.05 % Lignoceric acid: <0.2 %
Monounsaturated fats	Oleic acid: 55.0–83.0 % Palmitoleic acid: 0.3–3.5 %
Polyunsaturated fats	Linoleic acid: 3.5–21.0 % α-Linolenic acid: <1.0 %

Table 1.11. Fats in soybean oil (United States Department of Agriculture, Agricultural Statistics 2004)

Saturated fats	Stearic acid 4 % Palmitic acid 10 %
Monounsaturated fats	Oleic acid 23 %
Polyunsaturated fats	Alpha-Linolenic acid 7–10 % Linoleic acid 51 %

Table 1.12. Fats in sunflower oil (British Pharmacopoeia 2005)

Saturated fats	Palmitic acid 4 – 9 % Stearic acid 1 – 7 %
Monounsaturated fats	Oleic acid 14 – 10 %
Polyunsaturated fats	Linoleic acid 48 – 74 %

FHA is considered as a surfactant; because it contains both hydrophobic groups "Tail" which is hydrocarbon soluble (non-polar), and hydrophilic groups "Head" which is water soluble (polar), as show in Figure 1.6. Therefore, they are soluble in both organic solvents and water (Salager, 1999).

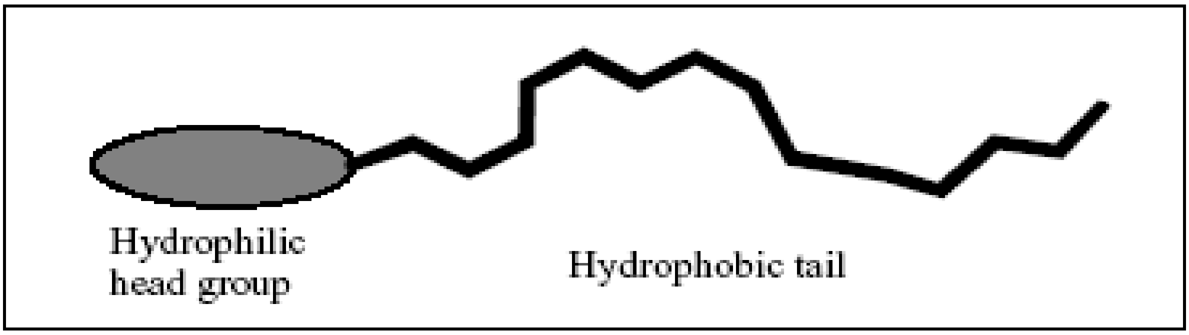


Figure 1.6. Surfactant molecule (Salager, 1999).

Surfactant compounds play an important role in many practical applications and products. They are often labeled according to their main use such as: soap, detergent, wetting agent, dispersant, emulsifier, foaming agent, bactericide, corrosion inhibitor and antistatic agent (Rieger, et al., 1997).

Surfactants are classified to anionic surfactants, cationic surfactants, zwitterionic surfactants (amphoteric), and nonionic surfactants (Pashley and Karaman, 2004). Because of their structures, their solutions have two common properties: surface adsorption and the ability to self assemble as micelles (Bozeya, 2008). Water, surfactant, and hydrocarbon oil can form structures called emulsion and microemulsion (Holmberg, et al., 2002).

1.2 Literature Review

1.2.1 Bentonite

Because of the wide chemical and physical properties of bentonite, it has a wide range of applications in several fields like: chemical, pharmaceutical and food industry, cosmetic products (filling material), civil and environmental engineering (sealing material), agriculture (soil conditioner, animal feeding) and metallurgy (Haddadin, 1974).

The abundance of bentonite in many areas around the world, and its low cost makes it a strong candidate for the removal of many pollutants. There are many research studies conducted on natural bentonite to study its potential as an adsorbent.

Cherouche, et al. (1997) investigated the efficiency of bentonite in removing lanthanum ions. They reported that natural bentonite is a promising adsorpent for heavy metal removal.

The interaction of organic substances with clay has a multitude of consequences that are reflected in the physical, chemical and biological properties of the soil matrix. In general, clays tend to stabilize organic matter, like what bentonite is used in asphalt emulsions, where it holds oil and water phases together in a stable emulsion, and there is a high correlation exists between the organic matter and clay contents of many soils. Some types of organic substances serve to bridge soil particles together, thereby forming stable aggregates (Stevenson, 1982).

Modification of bentonite by organic substances, increases its ability to adsorb/absorb certain heavy metals, and also organic compounds (Yu, et al., 2009). Vinod,

et al. (2003) investigated the adsorption of three dyes on the humic acid/bentonite complex at a pH of 5.0-7.0, and T = 30 °C.

Bentonite isolated from Maghnia (Algeria) have shown that the surface properties of bentonite can be greatly modified with surfactants by simple ion – exchange reaction, leading to Van der Waal's type interactions between organic surfactant cations and the adsorbate. As a result, the modified bentonite adsorption capacity increased dramatically in comparison to natural bentonite (Makhoukhi, et al., 2007).

1.2.2 Kaolin

The largest single user of kaolin is the paper industry, also as filler in many rubber goods, in ceramic products and insulators, and in paint because it is chemically inert and insoluble in the paint system.

The addition of kaolin to thermosetting and thermoplastic mixes gives smoother surfaces, a more attractive finish, good dimensional stability, and high resistance to chemical attack (Murray, 1961).

Kaolin in such sediments may show a higher selectivity for transition heavy metal ions due to the presence of pH dependent adsorption sites. Moreover, Davis, (1982) has shown that the reactive edge sites of kaolin may be coated with adsorbed organic matter, further enhancing metal ion adsorption capacity. Inorganic particles (e.g., kaolin) coated with humic substances play an important role in the environmental behavior of various ions (Hizal and Apak, 2006, a).

Typically, kaolin has a relative low cation-exchange capacity (CEC) [3–15 meq/100 g of clay] and smaller surface area ranged from 10 to 20 m^2/g (Adebowale, et al., 2006). So it is often modified from its natural state by physical or chemical treatments to enhance the properties of the material, and to improve its sorption capacity.

Similarly, when kaolin is modified by humic acid its ability to adsorbs certain metals from the environments increase (Gabbour, et al., 1998).

Kaolin, like most of the clay minerals, can intercalate various molecules in their interlayer space. Strong polar molecules can expand the basal spacing, which eventually leads to the rupture of the interlayer hydrogen bonds, or by either impregnation or grafting of organic/inorganic molecules on its surface (Unuabonah, et al., 2007).

Hence, the kaolin surface is expected to have two kinds of binding sites that could interact with metal ions via ion exchange and adsorption mechanisms. Natural clays as adsorbent with low cost have received much attention on heavy metals sorption from contaminated water (Jiang, et al., 2010).

Kaolin is an industrial mineral used primarily as inert filler and customers combine it with other raw materials in a wide variety of applications (Liu, et al., 2009). Kaolin is a soft, earthy, usually white mineral. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust color. Lighter concentrations yield white, yellow or light orange colors, like the Jordanian kaolin (El-Eswed, et al., 2009).

1.2.3 Fatty hydroxamic acids

Various Soviet and Russian scientists have found a variety of applications for such alkylhydroxamic acids, and they have reported methods for making alkylhydroxamic acids and their salts in alkaline aqueous media (Gorlovski, et al., 1965).

Shchukina, et al. (1970), reported a yield of only 72 to 78 % of the free $C_{7,9}$ hydroxamic acid by reacting the methyl ester with hydroxylamine sulfate, and sodium hydroxide for two hours at 20^o-25^o C and one hour at 55^o-60^o C, followed by acidification to pH 4-5 at temperatures below 40^o C. After that, several studies were carried out for synthesis of hydroxamic acids from different acids and esters with hydroxylamine (Griffith and Musher, 1973) (Pradip and Fuerstenau, 1984) (Thiery, et al., 1986).

Servat, et al. (1990) reported that the synthesis of alkanohydroxamic acids (N-acylhydroxylamines) using Mucor miehei lipase by reacting hydroxyl amine with the fatty acids obtained from different sources in their free or methyl ester form. Different parameters were studied such as temperature, molar ratio of reagents, quantity of biocatalyst and length of reaction. Dedy, et al. (2005) synthesized FHA from palm oil using immobilized lipase as a catalyst.

The fatty methyl/ethyl esters which are source for preparing FHA can be synthesized from oils using transesterification reaction where the triglycerides reacts with alcohols (methanol, ethanol or any alcohol) to form esters and glycerol (Ma and Hanna, 1999). The reaction rate and yield can be improved by using catalysts. Two type of catalysis are employed, alkali-catalyzed and acid-catalyzed transesterification. The alkali-catalyzed transesterification is much faster than the acid-catalyzed. Transesterification

reactions are reversible reactions; excess alcohol is required to shift the equilibrium to the products side (Sharma, et al., 2008).

Hydroxamic acids have the capability to chelates with ferric ion which can be used for medical purposes and as siderophore models (Araki, et al., 1987). In recent years, hydroxamic acids derivatives have received a great attention due to their biological activity as growth factors, food additives, antibiotics, antifungal agents, cell division factor and metal chelators (Rothenberg, et al., 1999). Alkylhydroxamic acids and their salts are good collectors for the froth flotation of oxide minerals or metals such as pyrochlore, calcite, and malachite (Miller, et al., 2002). They are generally more powerful and more selective in attaching to the clay minerals than the conventional fatty acids, fatty amines, petroleum sulfonates and alkyl sulfates (Hughes, et al., 2007).

The hydrophilicity of clay minerals towards organic polymers is high. This makes it unuseful for industrial applications. By decreasing the hydrophilicity towards polymers this will open up new horizon in polymer composite material that has high chemical and physical properties (Fellahi, et al., 2001).

The general method to make polymer/clay composites is to modify the clay's surface with surfactants, and then the polymer and the modified clay mixed together under high shear at a temperature above the melting point of the polymer (Fellahi, et al., 2001).

The modification of natural clay may be carried out via exchanging the original interlayer cations with organic cations where they are transformed from organophobic to organophilic materials, this significantly increase the basal spacing of the clay layers (Giannelis, 1998). It is generally accepted that the extent of swelling depends on the length of the alkyl chain and the cation exchange capacity of the clay (Zidelkheir and Abdelgoad, 2008).

Processing and properties of Poly Lactic Acid (PLA)/thermoplastic starch/montmorillonite nanocomposites show improvement in the tensile modulus and strength and a reduction in fracture toughness (Arroyo, et al., 2010). Plasticized PLA-based nanocomposites were prepared and characterized with polyethylene glycol and montmorillonite. It is reported that the organo-modified montmorillonite-based composites have shown the possible competition between the polymer matrix and the plasticizer for the intercalation between the aluminosilicate layers (Paul, et al., 2003).

Al-Mulla, et al. (2010) studied a new biopolymer nanocomposites based on Epoxidized Soybean Oil (ESO) plasticized poly(lactic acid)/modified clay by Fatty Nitrogen Compounds (FNCs), were its results show higher thermal stability and significant improvement of mechanical properties, as shown in Figure 1.7.

The incorporation of organoclays in the polymer to produce a nanocomposite is another means to modify the property balance of a material. The improvements in thermal stability, physical and mechanical properties can be achieved by addition of 2–5 % weight of organoclays in comparison to the neat polymer (Kulinski and Piorkowska, 2005) (Ren, et al., 2006).

The presence of long-chain (mainly 16 and 18 carbon atoms) in FHAs containing O and N atoms suggests that the FHAs should be very useful as surfactants for clay modification. Using of FHAs, which are considered renewable resources and environmentally friendly reduces the dependence on petroleum-based surfactants. This method will increase the compatibility of clays to be mixed with various types of polymer that might have potential applications in polymer industry and increase its chemical and physical properties, and this is important for many chemical industries as they are derived

from renewable, biodegradable, environmentally friendly and easily available raw materials.

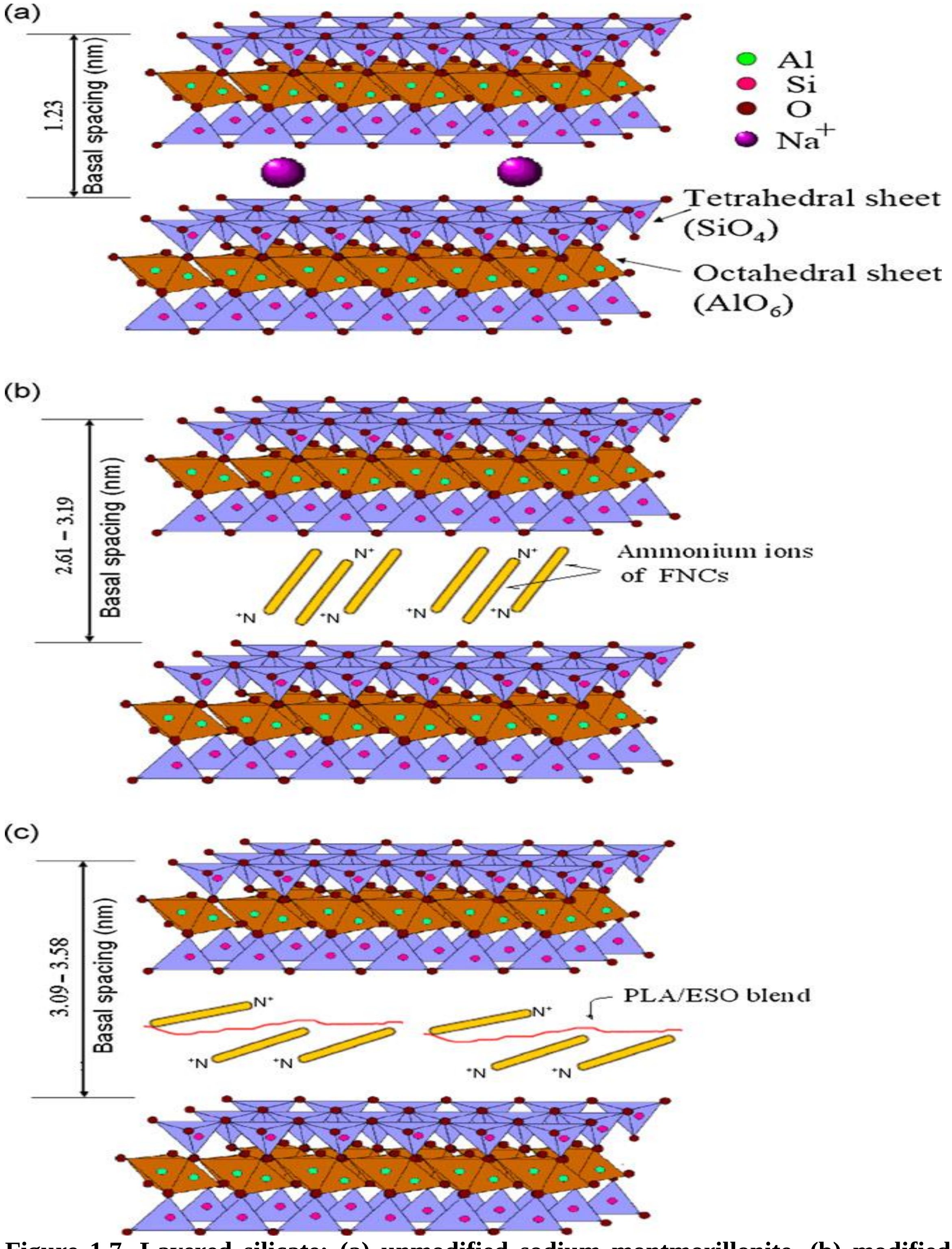


Figure 1.7. Layered silicate: (a) unmodified sodium montmorillonite, (b) modified sodium montmorillonite by FNCs and (c) PLA/ESO nanocomposites (Al-Mulla, et al., 2010).

The Aim of the Present Study

To our knowledge there have been no studies on modification of Jordanian clay (Kaolin and Bentonite) using Fatty Hydroxamic Acids (FHA) prepared from several vegetable oils.

There for the steps with present study are:

1. The Fatty Hydroxamic Acid (FHA) will be synthesized via chemical methods from different vegetable oils which are:
   A) Corn oil
   B) Olives oil
   C) Palm oil
   D) Soybean oil
   E) Sunflower oil
2. Characterization the FHA by FT-IR and mass spectroscopy.
3. Characterization The Jordanian clays (Kaolin and Bentonite) by FT-IR, XRD, and SEM.
4. Modification of the Jordanian clays (Kaolin and Bentonite) with FHAs.
5. Characterization the new composite materials by FT-IR, XRD, and SEM.
6. Comparison the efficiency of modification between the different sources and all of the new composite materials.

CHAPTER

TWO

MATERIAL

INSTRUMENTS

AND

EXPEREMINTAL

2.1 Materials and chemicals

The various types of vegetable oils were purchased from Universal Modern Industries Company (UMIC) Jordan, and clays were provided from Geology Department, University of Jordan. All of chemicals had been used are listed in Table 2.1.

Table 2.1. Chemicals that had been used.

Chemicals	Grade	Company
Hydroxylamine hydrochloride	98 %	AVONCHEM, UK
Sodium Chloride	99 %	LOBA CHEMIE, India
Ferric Chloride hexahydrate	98 %	BDH Chemicals Ltd., England
Copper(II) Sulphate pentahydrate	98 %	BDH Chemicals Ltd., England
Sodium hydroxide	98 %	CARLO ERBA REACTIFS, France
Hydrochloric acid	37 %	TEDIA, USA
Methanol	99.6 %	Gainland Chemical Company, UK
Ethanol	99.5 %	Gainland Chemical Company, UK.
Diethyl ether	99.5 %	Gainland Chemical Company, UK.
Hexane	HPLC grade	May&Baker, UK.

2.2 Instrumentation

2.2.1 Fourier transform infrared (FT-IR) spectrophotometer

FT-IR spectra were recorded using Thermo Nicolet NEXUS 670 FT-IR Spectrophotometer. KBr Powder was dried at 200 °C for 24 h, and then KBr was homogenized with all samples (1:100) in ball grinder. The disc (diameter 1 cm, thickness 0.1 cm) was prepared using hydraulic press. The infrared spectrum was recorded in the wave-number range 400 - 4000 cm^{-1}.

2.2.2 High resolution mass spectrometry (HRMS)

HRMS spectra were recorded using BRUKER APEX IV. The methanol HPLC-grade (Riedel-deHaen Chemical Co. Germany) was used as a solvent for all of the samples.

2.2.3 Scanning electron microscope (SEM)

Electron microscopy techniques have been used to obtain information on the morphology and size of the sample by scanning electron microscopy (SEM). The morphology was studied using FEI inspect F50 scanning electron microscope operated at accelerating voltages of 2 kV with magnification of 15000 **X**. The particles were glued to a metallic sample holder using a carbon double-side tape and then coated with platinum to

prevent the charging effect. The energy dispersion spectrum (EDS) model Bruker AXS with drift silicon detector was used to determine the elements present.

2.2.4 Ultra violet visible (UV-VIS) spectrophotometer

UV-VIS CARY 100 VARIAN spectrophotometer was used to identify the λ_{max} within the wavelength ranged (200-900 nm) to FHA/Fe (III) complex and measuring the absorption intensity for all samples that consists of FHA. A quartz standard cell was used in this technique.

2.2.5 X-ray diffraction (XRD)

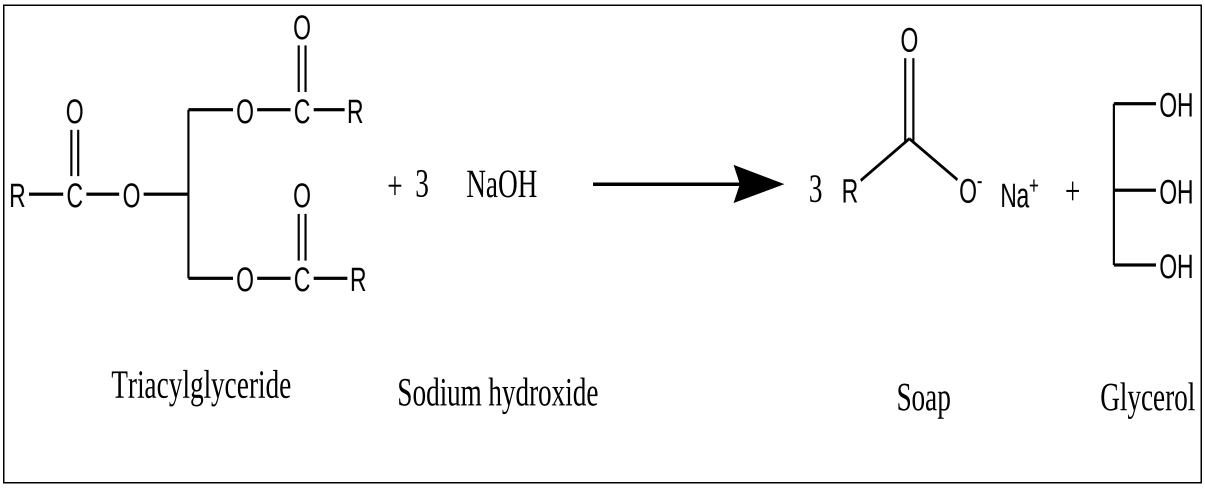
XRD samples were recorded using Philips model PW1830, operated at 40 KV and 30 mA. The diffractometer employing Cu-K_{α} radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The Cu-K_{α} radiation was generated by a Philips glass diffraction X-ray tube broad focus 2.7 kW type. All samples were mounted on samples holder and the basal spacing was determined via powder technique.

2.3 Experimental

2.3.1 Determination of average molar mass of (FA) in vegetable oils

The average molar mass of various vegetable oils was calculated by back titration technique as following:

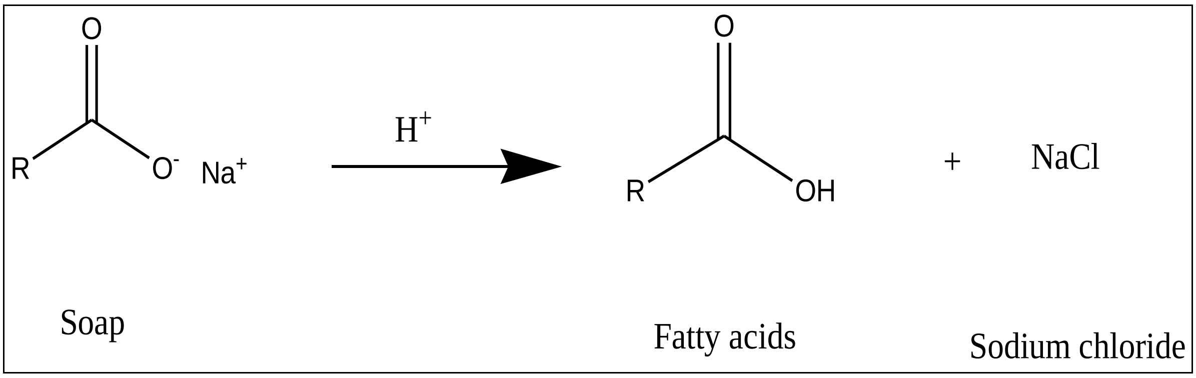
A 3.0000 g of sodium hydroxide were dissolved in 50.00 mL of distilled water, added slowly to a 10.00 mL of previously warmed vegetable oil. The mixture was heated to boiling until the saponification reaction was completed by forming a solid. The solid was filtrated, added to 25.00 mL of saturated solution of sodium chloride, then heated for 15 minutes, and filtrated again. This step was repeated three times, to remove glycerol, and any other traces of sodium hydroxide from the soap. The filtrate solution was titrated with 0.2 M of potassium hydrogen phthalate (KHP) M.m= 204.22 g/mol using phenolphthalein as indicator. The reaction is shown in Scheme 2.1.



Scheme 2.1. The reaction equation of triacylglyceride with sodium hydroxide

2.3.2 Preparation of FA

The solid soap prepared in the previous step was dissolved in 50.00 mL of distilled water, put in ice bath for about 30 minutes, a concentrated hydrochloric acid was added very slowly with stirring until the solution became acidic using a litmus paper. The FA was separated by adding 20.00 mL hexane using a separatory funnel. The upper layer was washed three times with 20.00 mL of saturated solution of NaCl, to remove any traces of remaining HCl. The reaction is shown in Scheme 2.2.



Scheme 2.2. The reaction equation of acidification of soap.

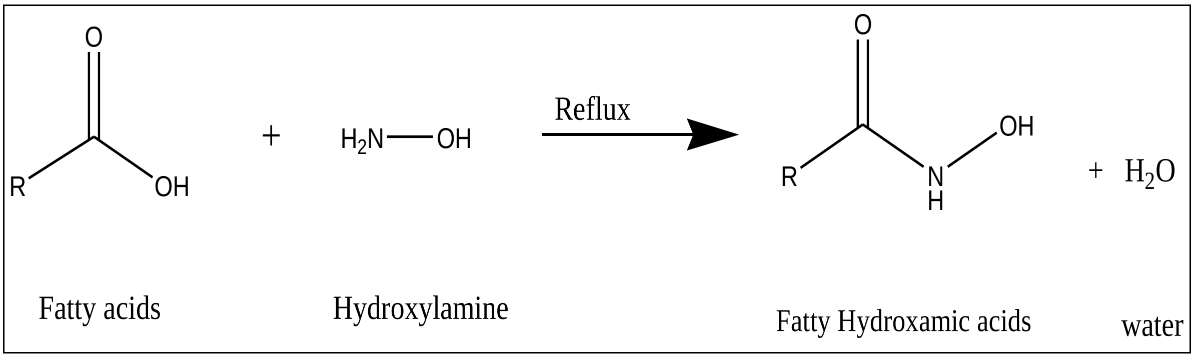
2.3.3 Preparation of FHA

The FHA was prepared by three different methods:-

2.3.3.1 Preparation of FHA from FA

The FA was dissolved in hexane with hydroxylamine hydrochloride by reflux at boiling point of hexane for 6 h, by using a thermostated round bottom flask, equipped with water cooled condenser, and mechanical stirrer. After the reaction finished (the product changed color to green with copper (II) due to its ability to form complex). The product

was dissolved in hot hexane, and separated from bottom layer using separating funnel. The hexane phase was cooled in an ice bath for 4 h to obtain FHA, then filtrated and washed by hexane for three times, then the product was recrystallized by hexane, finally it dried in a vacuum desiccators over phosphorous pentoxide. The reaction is shown in Scheme 2.3.

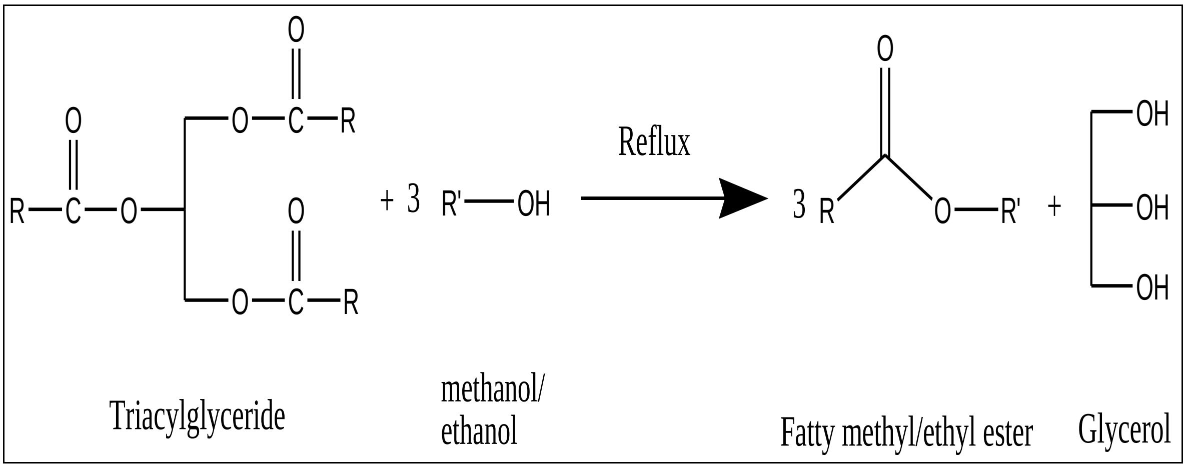


Scheme 2.3. The reaction equation of FA with hydroxylamine

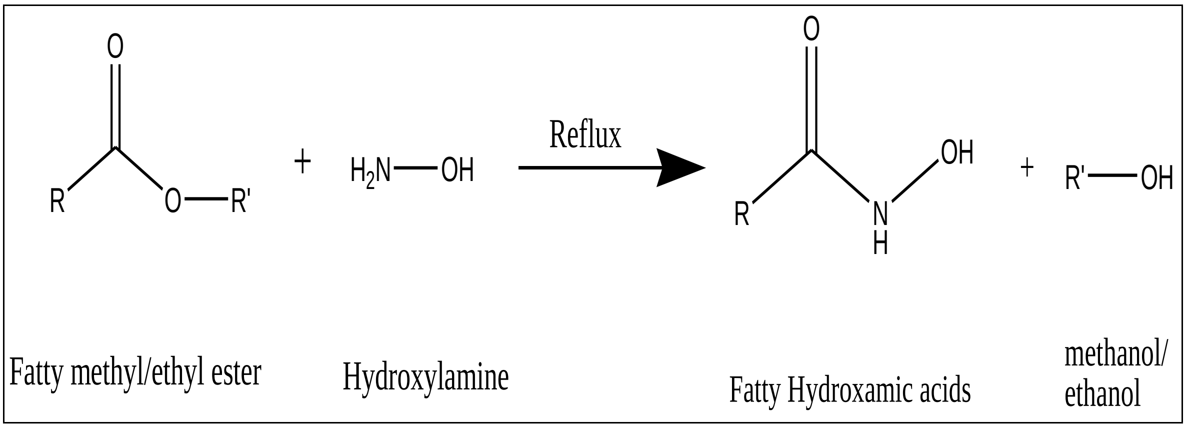
2.3.3.2 Preparation of FHA from methyl and ethyl fatty ester

The methyl and ethyl fatty ester were prepared using transesterification reaction method which had been done by adding methoxide/ethoxide to warmed oil with continuous stirring for 5 h (Ma and Hanna, 1999). The reaction is shown in Scheme 2.4. Then the product separated and dissolved in hexane with hydroxylamine hydrochloride by reflux at boiling point of hexane for 12 h, by using a thermostated round bottom flask, equipped with water cooled condenser, and mechanical stirrer. After the reaction finished (the product changed color to green with copper (II) due to its ability to form complex). The product was dissolved in hot hexane, and separated from bottom layer using separating funnel. The hexane phase was cooled in an ice bath for 4 h to obtain FHA, then filtrated and washed by hexane for three times, then the product was recrystallized by

hexane, finally it dried in a vacuum desiccators over phosphorous pentoxide (Hoidy, et al., 2010). The reaction is shown in Scheme 2.5.



Scheme 2.4. The reaction equation of transesterification

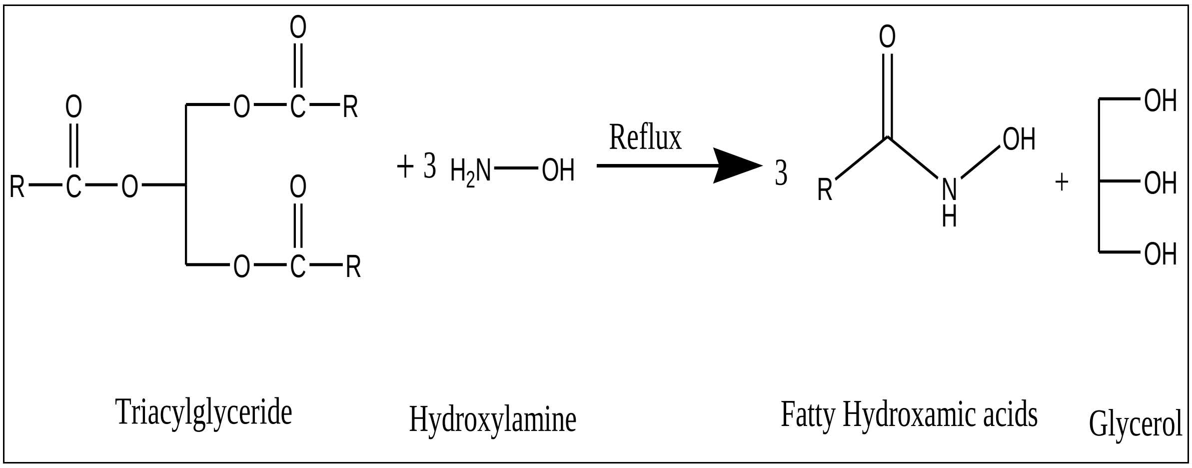


Scheme 2.5. The reaction equation of fatty methyl/ethyl ester with hydroxylamine

2.3.3.3 Preparation of FHA directly from vegetable oils

The oil was dissolved in hexane with hydroxylamine hydrochloride by reflux at boiling point of hexane for 10 h, by using a thermostated round bottom flask, equipped with water cooled condenser, and mechanical stirrer. After the reaction finished (the product changed color to green with copper (II) due to its ability to form complex).

The product was dissolved in hot hexane, and separated from bottom layer using separating funnel. The hexane phase was cooled in an ice bath for 4 h. to obtain FHA, then filtrated and washed by hexane for three times, then the product was recrystallized by hexane, finally it dried in a vacuum desiccators over phosphorous pentoxide (Hoidy, et al., 2010). The reaction is shown in Scheme 2.6.



Scheme 2.6. The reaction equation of triacylglyceride with hydroxylamine

2.3.4 Purification of Al-Azraq Bentonite

The main aim of this purification is to remove quartz. This process was done using the following steps; firstly, the bentonite samples of particle size less than 250 µm were mixed with distilled water and then the suspension was centrifuged at 750 rpm to obtain particles less than 2 µm. Carefully, these particles were separated in large bottles. The centrifugation was repeated for further five times more (Salman, et al., 2007). The centrifuged (pure) bentonite samples were dried in an oven at 105 ^{o}C for 24 hours and stored in polyethylene bottles.

2.3.5 Calibration curve of FHA

Several masses of FHA were dissolved to 100 mL of 70 % ethanol, and then 1 mL of each solution added to 10 mL of $FeCl_3$ solution (70 % ethanol) were detected by UV-VIS spectrophotometer. The full scanning of FHA on UV-VIS spectrophotometer showed that the absorption decreased when the mass of FHA decreased at wavelength 520 nm which is the λ max, as shown below in Figures 2.1 and 2.2. Depending of that value, all of the various samples were prepared with different weights and theirs absorptions are shown below with theirs calibration curve in Table 2.2 and Figure 2.3 respectively.

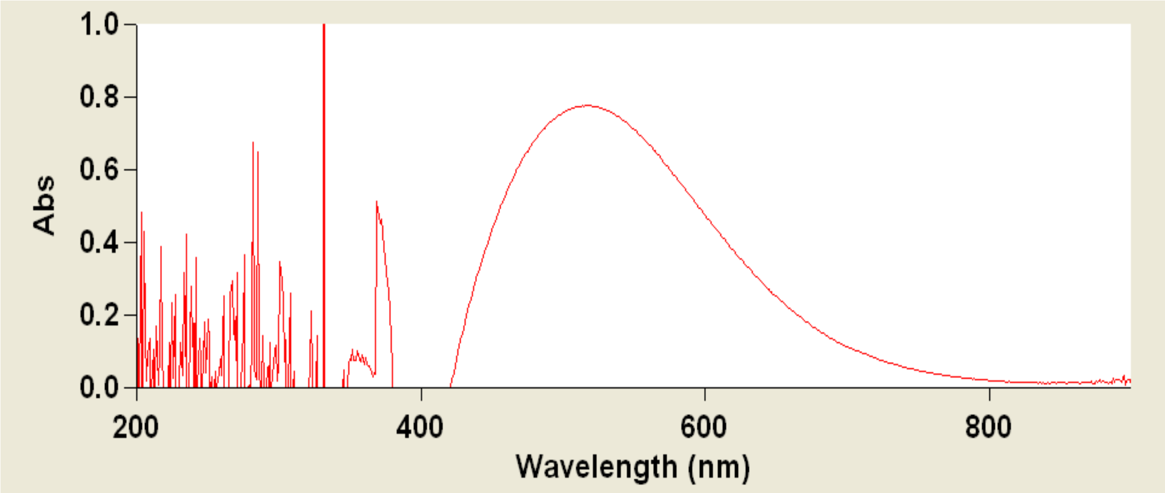


Figure 2.1. Spectrum of UV-VIS spectrophotometer for 0.5 g of palm FHA

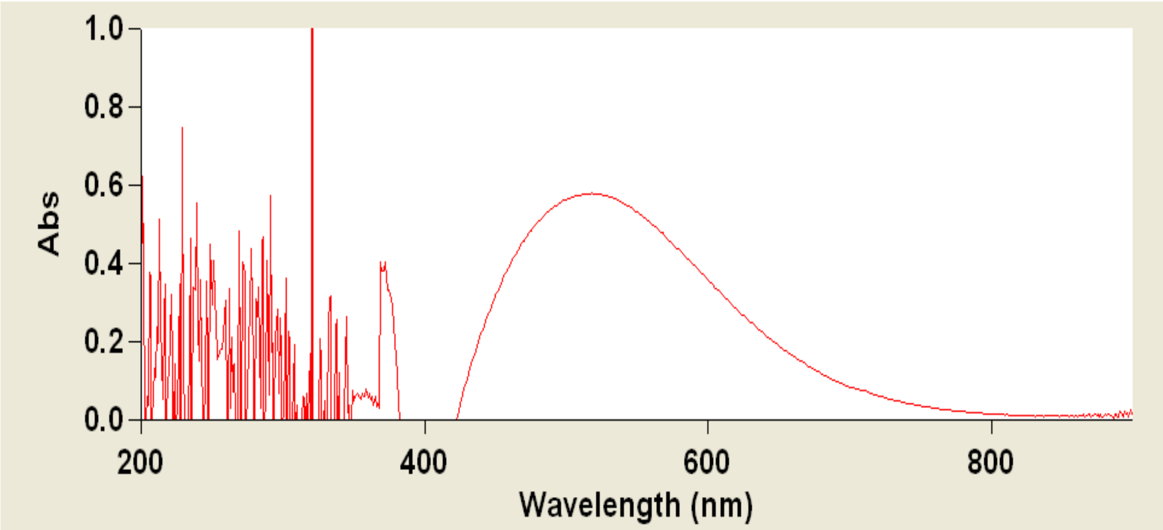


Figure 2.2. Spectrum of UV-VIS spectrophotometer for 0.4 g of palm FHA

Table 2.2. Several weights of FHA with theirs absorptions at wavelength 520 nm.

Number	Mass of FHA (g)	Absorption
1	0.1183	0.254
2	0.2401	0.363
3	0.3351	0.488
4	0.4132	0.585
5	0.5353	0.785

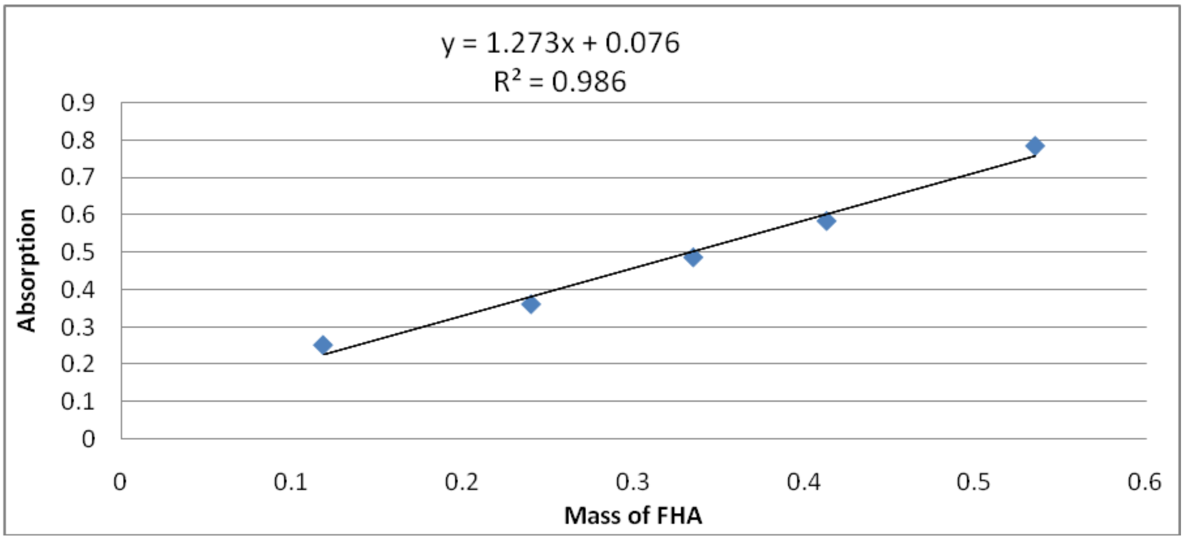


Figure 2.3. Calibration curve of FHA.

2.3.6 Preparation of modified clays with FHA/S

Around 0.5 g of each of FHA/S was dissolved in 100 mL of 70 % ethanol and around 1g of every each clay was added to the solution stirred at room temperature for several of times. The effect of time studied by taking 1ml of the each solution by pipet different times which are before, after 1 , 3 , 6 , 12 , 18 , 24 and 48h . Every 1 mL was reacted with 10 mL of $FeCl_3$ solution in 70 % ethanol to give colored solution. All of the samples were detected by UV-VIS spectrophotometer at wavelength 520 nm. The remaining mixtures of each solution were filtered, and the samples with maximum uptake were detected by FT-IR, SEM and XRD.

CHAPTER

THREE

RESULTS

DISCUSSIONS

AND

CONCLUSIONS

3.1 Average molar mass of FA in vegetable oils and the percentage yield of FHA

The average molar mass of various vegetable oils were calculated by back titration technique and the results are listed in Table 3.1. The percentage yields of FHA obtained from the three synthetic methods are listed in Table 3.2.

Table 3.1. Average molar mass of several vegetable oils (g/mol).

Corn oil	Olive oil	Palm oil	Soybean oil	Sunflower oil
560	510	435	480	545

Table 3.2. Percentage yield of FHA produced from several vegetable oils by three synthetic methods.

Method	Corn (%)	Olive (%)	Palm (%)	Soybean (%)	Sunflower (%)
1	83	80	88	75	75
2	80	78	85	70	68
3	86	84	92	82	82

3.2 HRMS spectrometry for FHA

From data of HRMS spectrometry were identified the types of all FA in every types of vegetable oils and the molecular mass of FHA by detecting the nitrogen atom, and it was showed that some of the FHAs products contained some unreacted compounds after the recrystallization process; that's because the polarity of reactants and products are close to each others. Moreover, the data like in Figures 3.1 and 3.2 showed that the FHA products contained a mixture of compounds, which are listed in Table 3.3.

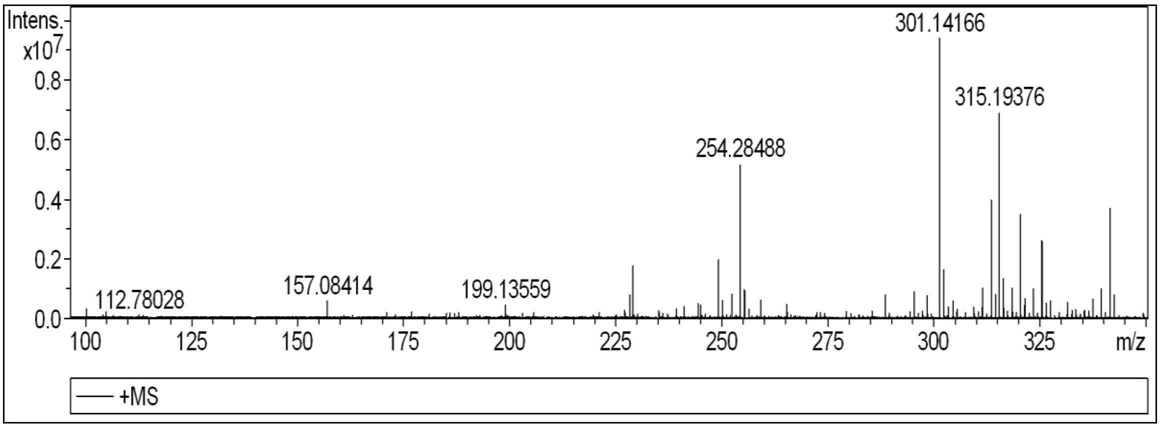


Figure 3.1. Positive mass spectrum for olive FHA.

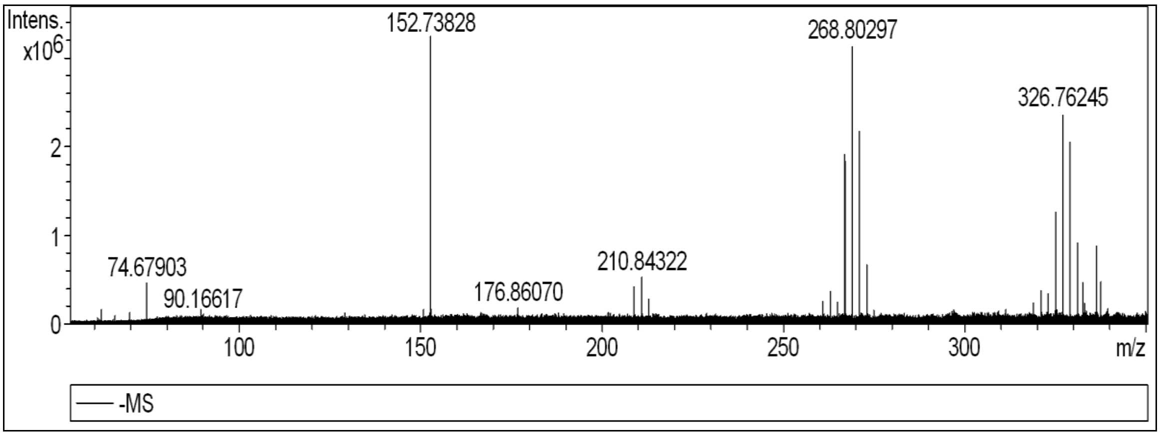


Figure 3.2. Negative mass spectrum for olive FHA.

Table 3.3. FHA synthesized from some vegetable oils.

Vegetable oils	Common name	Chemical formula	Molecular mass
Corn	Linoleic hydroxamic acid	$C_{18}H_{33}NO_2$	295
	Linolenic hydroxamic acid	$C_{18}H_{31}NO_2$	293
	Oleic hydroxamic acid	$C_{18}H_{35}NO_2$	297
	Palmitic hydroxamic acid	$C_{16}H_{33}NO_2$	271
Palm	Palmitic hydroxamic acid	$C_{16}H_{33}NO_2$	271
	Oleic hydroxamic acid	$C_{18}H_{35}NO_2$	297
	Stearic hydroxamic acid	$C_{18}H_{37}NO_2$	299
Olive	Stearic hydroxamic acid	$C_{18}H_{37}NO_2$	299
	Arachidic hydroxamic acid	$C_{20}H_{41}NO_2$	327
Soybean	Linoleic hydroxamic acid	$C_{18}H_{33}NO_2$	295
	Linolenic hydroxamic acid	$C_{18}H_{31}NO_2$	293
	Oleic hydroxamic acid	$C_{18}H_{35}NO_2$	297
	Palmitic hydroxamic acid	$C_{16}H_{33}NO_2$	271
Sunflower	Linoleic hydroxamic acid	$C_{18}H_{33}NO_2$	295
	Oleic hydroxamic acid	$C_{18}H_{35}NO_2$	297
	Palmitic hydroxamic acid	$C_{16}H_{33}NO_2$	271

3.3 FT-IR spectrometry for FHA samples

All of FHAs were prepared from several vegetable oils were analyzed by FT-IR spectroscopy. The spectra are shown in Figures 3.3, 3.4 and 3.5 and the data summarized in Table 3.4. The FT-IR spectra for FHA exhibit characteristic absorption bands for the major functional groups involved in aliphatic alkyl chains. Figures 3.3–3.5 show the FT-IR spectra for all of FHA, where the absorption bands around 720 cm^{-1} indicates $[-CH_2-]_n$ rocking of the methylene groups. The absorption bands of bending vibrations around the regions 1460 - 1380 cm^{-1} are indicative of ($-CH_2$ and $–CH_3$) groups. Also the absorption bands around the regions 3010-2850 cm^{-1} are assignable to (=CH, -CH, $-CH_2$ and $-CH_3$) carbon-hydrogen stretching vibrations of the aliphatic alkyl chains (Jiang and Ng, 2006). The absorption bands around the regions 1115-975 cm^{-1} are assignable to C-N stretching. The absorption bands around the regions 1740-1630 cm^{-1} can be assigned to C=O stretching for amide and carboxylic, also to C=N. The absorption bands around the regions 3260-3240 cm^{-1} are assignable to O-H stretching for amide and carboxylic acid.

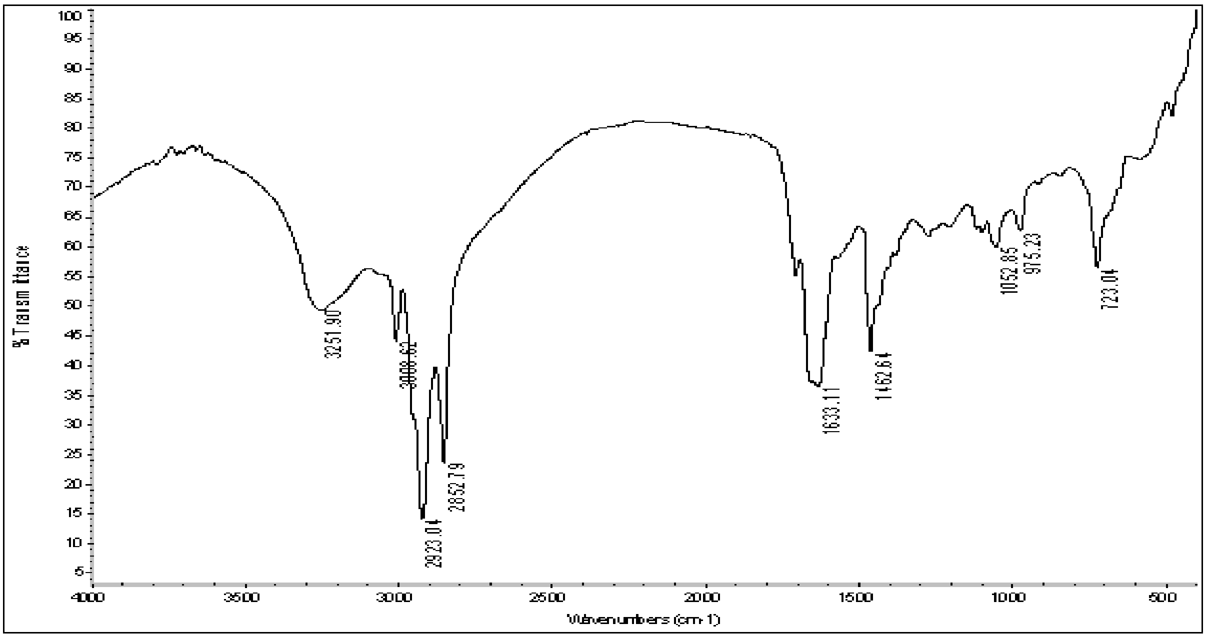


Figure 3.3. FT-IR spectrum of corn FHA

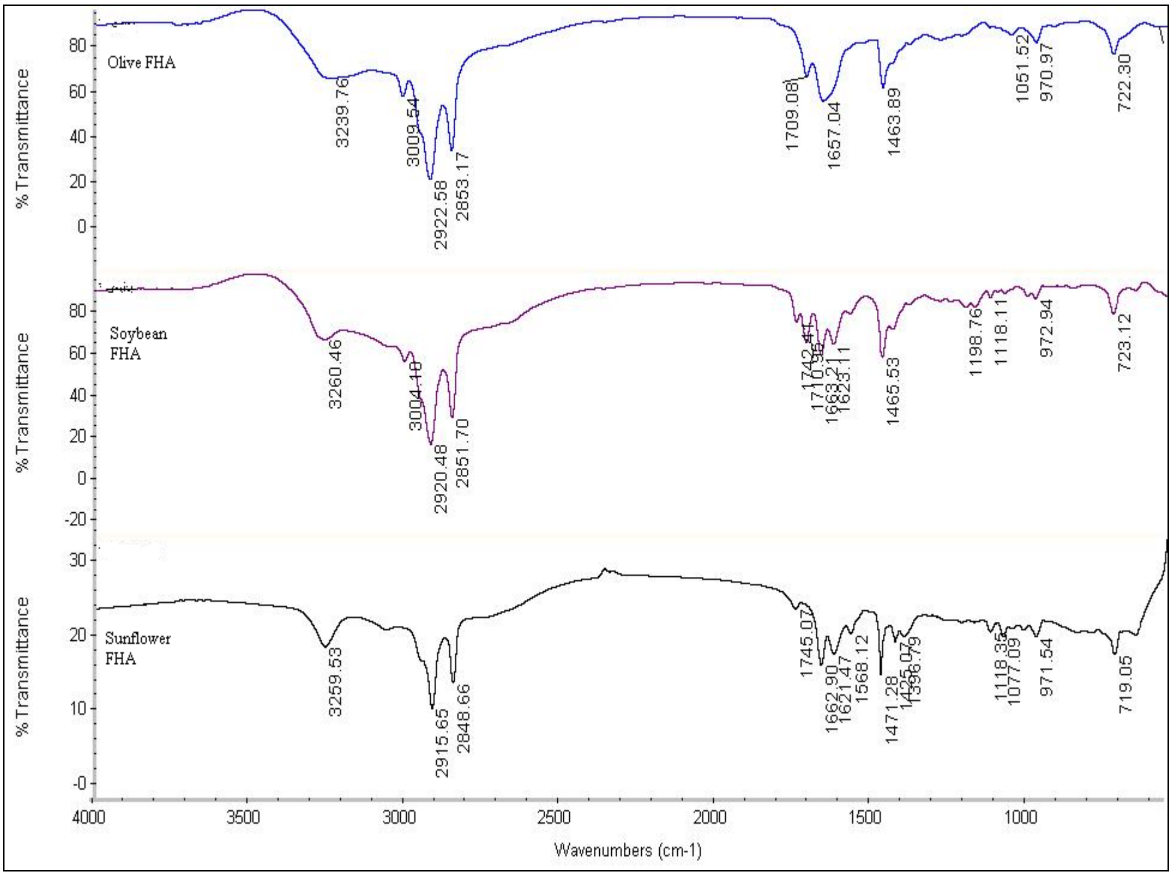
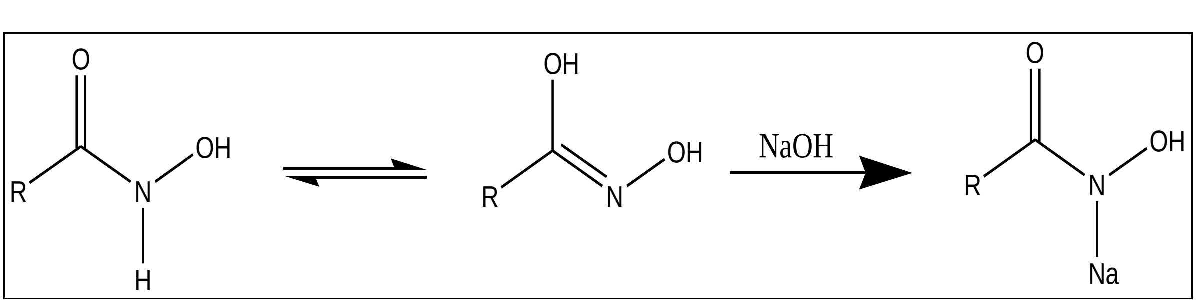


Figure 3.4. FT-IR spectrs of olive, soybean and sunflower FHA, respectively

This data proves that the FHA was prepared as a mixture with some unreacted compounds, and also all of FHAs have the tautomer isomerism structure of hydroxamic acid, which has more stability, as shown in Scheme 3.1. Figure 3.5 shows the FT-IR spectra for palm FHA and palm FHS respectively, where all of the absorption bands in FHS spectrum made right-shift and the N-H absorption band appeared around the region 3420 cm^{-1} as N-Na band.



Scheme 3.1. Tautomer isomerism structure of hydroxamic acid and structure of FHS

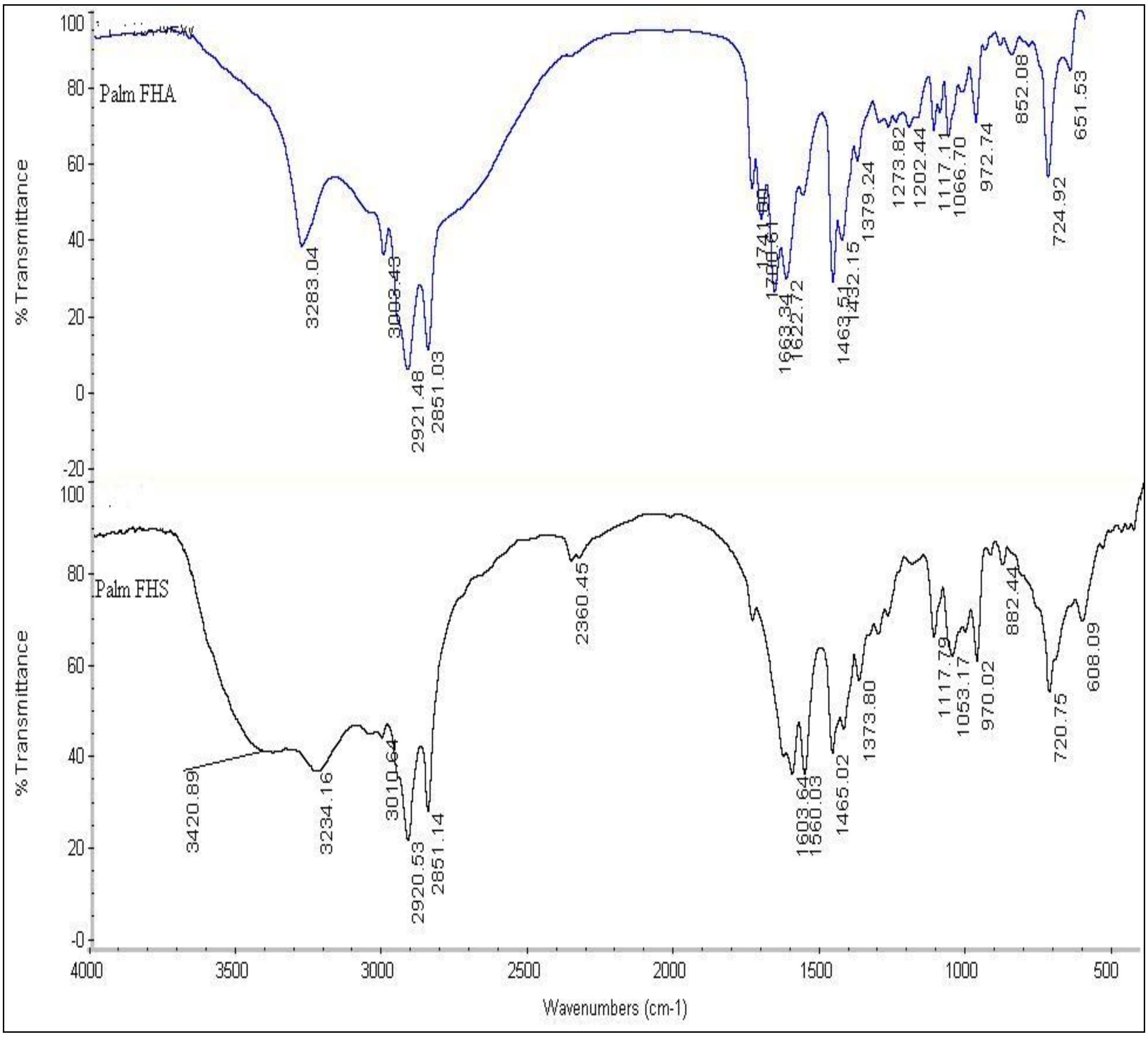


Figure 3.5. FT-IR spectra of palm FHA and palm FHS, respectively

Table 3.4. Assignment of FT-IR bands in FHA/S spectra.

Wavenumber (cm^{-1})	**Assignment**
3420	N-H stretching for amide
3260-3240	O-H stretching for amide
1460 - 1380	C-H bending
3010-2850	C-H stretching of alkyl
1740 - 1630	C=O stretching for amide
1115-975	C-N stretching

3.4 FT-IR spectrometry for unmodified and modified clays

Figures 3.6, 3.7 and 3.8 show the IR spectra of the White Kaolin (WK), Red Kaolin (RK) and Bentonite (Ben), and their modified species.

The bands at 3621-3698 cm^{-1} can be assigned to the terminal silanol-OH and to the bridge Si-OH-Si(Al) or to the hydrogen bonded Si(Al)OH. The broad bands at 3449-3487 cm^{-1} can be assigned to the OH stretching vibrations (ν_{OH}), which may arise from the isomorphic substitution in the tetrahedral and octahedral layers of the clays (Wilson, 1994). Moreover, some of these bands appear to have slightly shifted to higher wave numbers in the modified forms, in comparison to the unmodified clays.

The bands at 2853-2926 cm^{-1} appearing in the modified species only could be attributed to the symmetric and asymmetric stretching vibrations of the methylene (ν_{CH_2}), belonging to the organic modifier HFA. The bands at 1622-1633 cm^{-1} could be attributed to the OH deformation of water molecules β(H_2O) that have shifted to higher wave numbers as compared to molecular water (Farmer, 1974) (Gadsden, 1975).

The bands at 913-1109 cm^{-1} that appear as strong bands or as prominent shoulders can be assigned to the symmetric (ν_{sym} Si-O-Si) or asymmetric (ν_{asym} Si-O-Si(Al)) stretching vibrations. The bands at 694-796 cm^{-1} are characteristic of quartz and those at 428-539 cm^{-1} can be attributed to β(Si-O-Si(Al)) or β (Si-O-Si) bending vibrations (Marcel, 1967).

Figure 3.8 shows the FT-IR of samples obtained in acidic and basic medium. It can be seen from the spectrum that the intensity of absorption band of the methylene (ν_{CH_2}), of the sample prepared in acidic medium is greater than that obtained in basic medium.

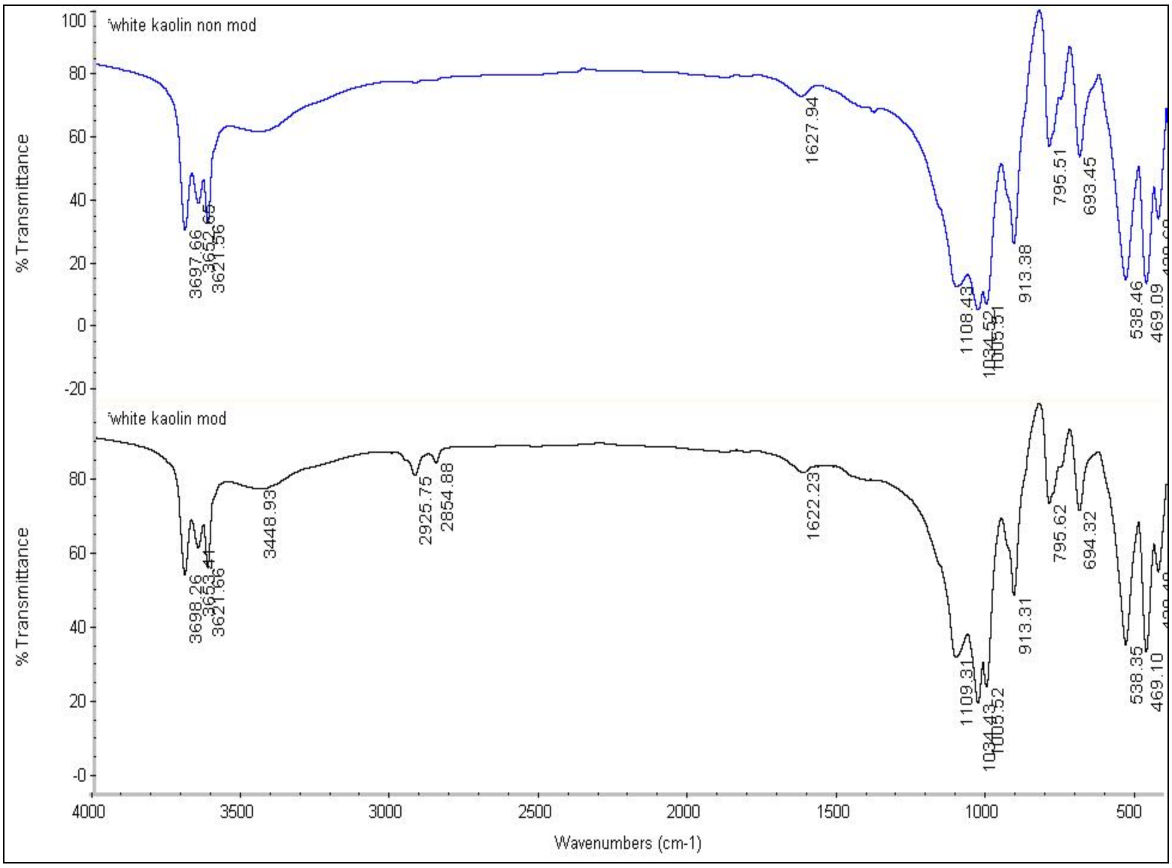


Figure 3.6. FT-IR spectra of unmodified and modified WK by FHA, respectively

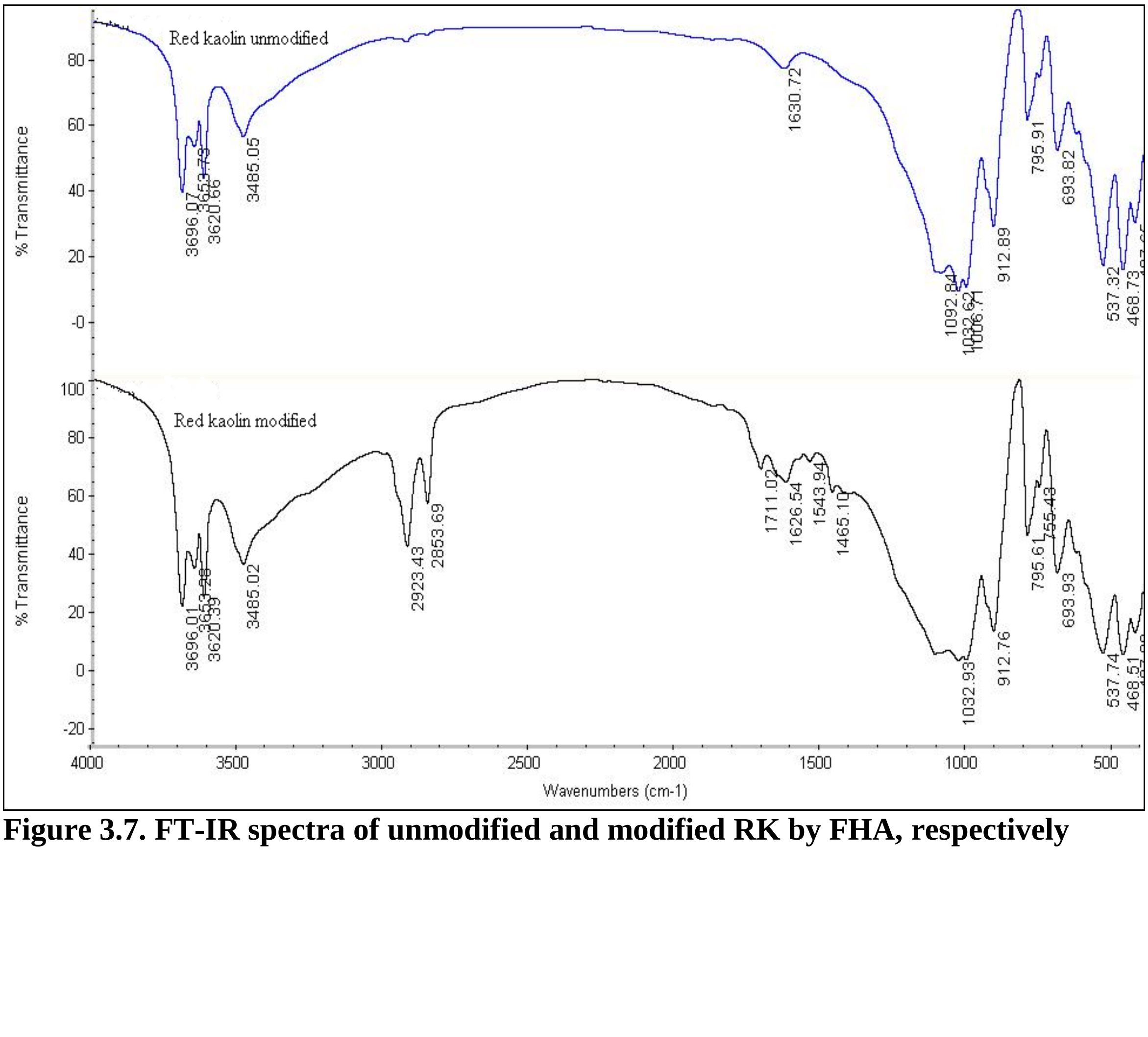


Figure 3.7. FT-IR spectra of unmodified and modified RK by FHA, respectively

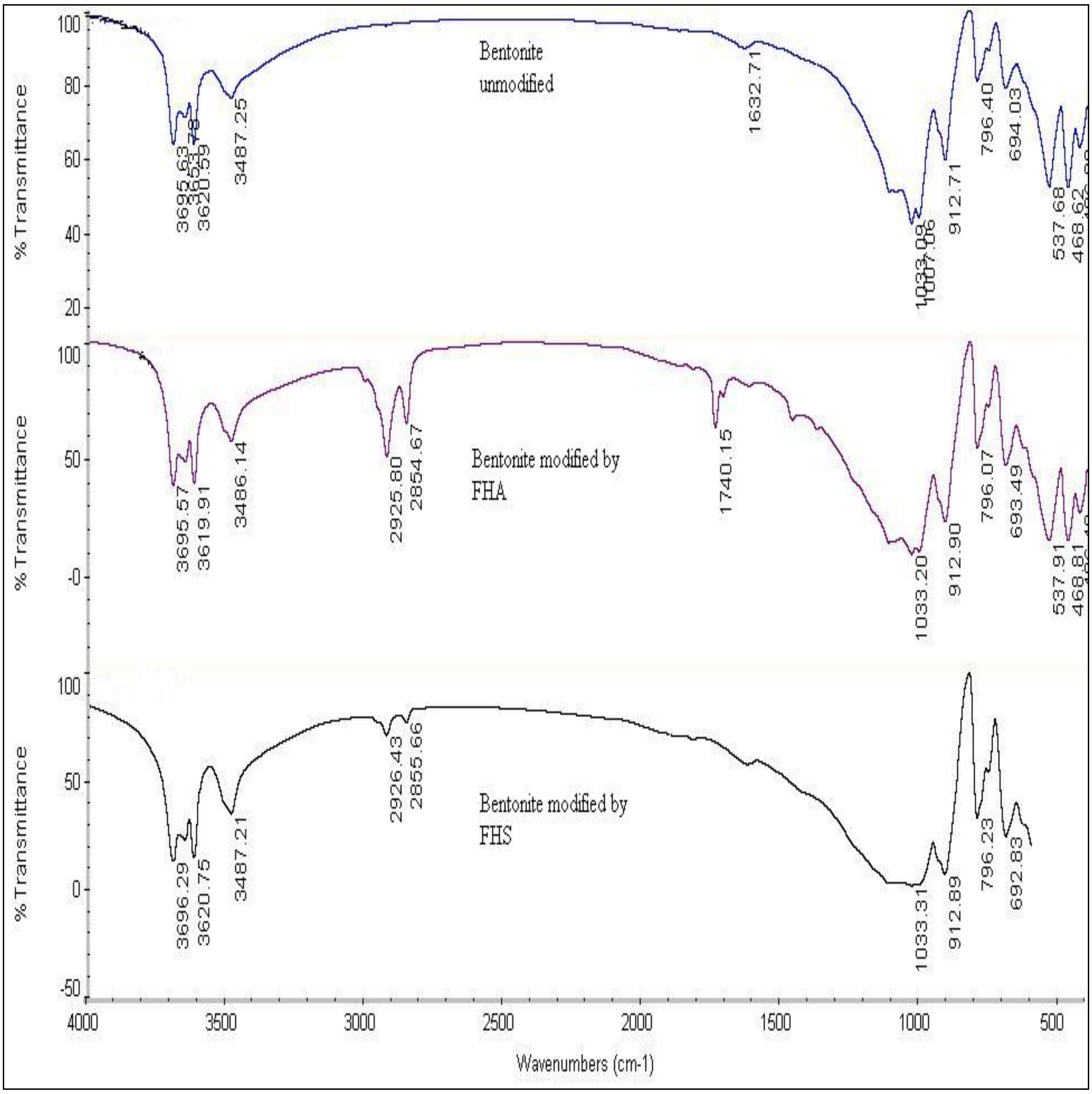


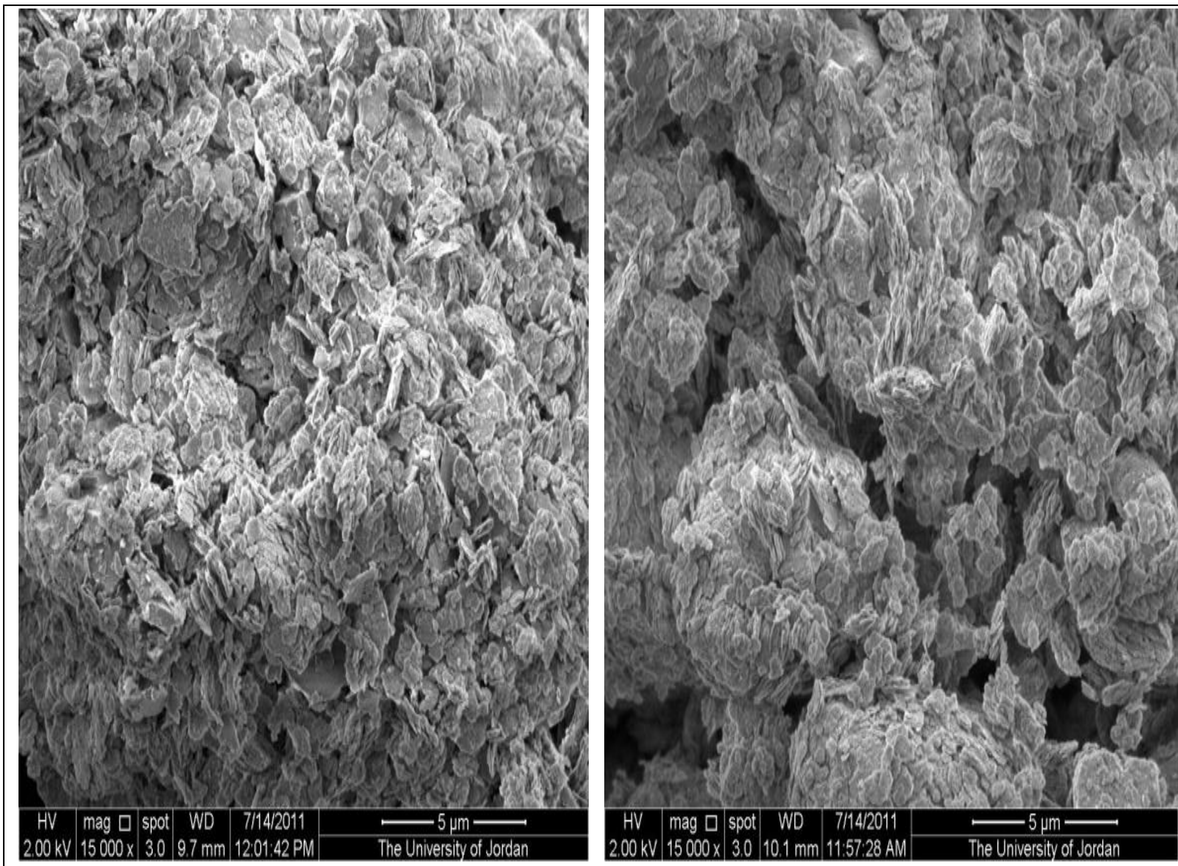
Figure 3.8. FT-IR spectra of unmodified and modified Ben by FHA and FHS, respectively.

3.5 Surface Morphology/ SEM Analysis

The surface morphology of the unmodified and modified bentonite, white kaolin and red kaolin was studied by using scanning electron microscopy (SEM). The scanning electron micrographs of the unmodified samples and their modified forms were obtained.

Figures 3.9, 3.10 and 3.11 are giving a clear picture of the surface morphology of these samples at 15000 magnifications, showing clearly the porous nature of these samples surfaces with sieve like structure of the bentonite and kaolins which are surrounded by small particle size clay materials. The modified clays by FHA electron micrographs, presented in Figures 3.9 – 3.11 at similar magnification, display some modification of the surface texture.

In both micrographs of the modified clays it can be noted that the modifier has coated most of the pores and edges. In the modified forms, large particles of the modifier can be seen on the surface as highly charged appearance.



(a) (b)

Figure 3.9. SEM micrographs for WK (a) unmodified (b) modified.

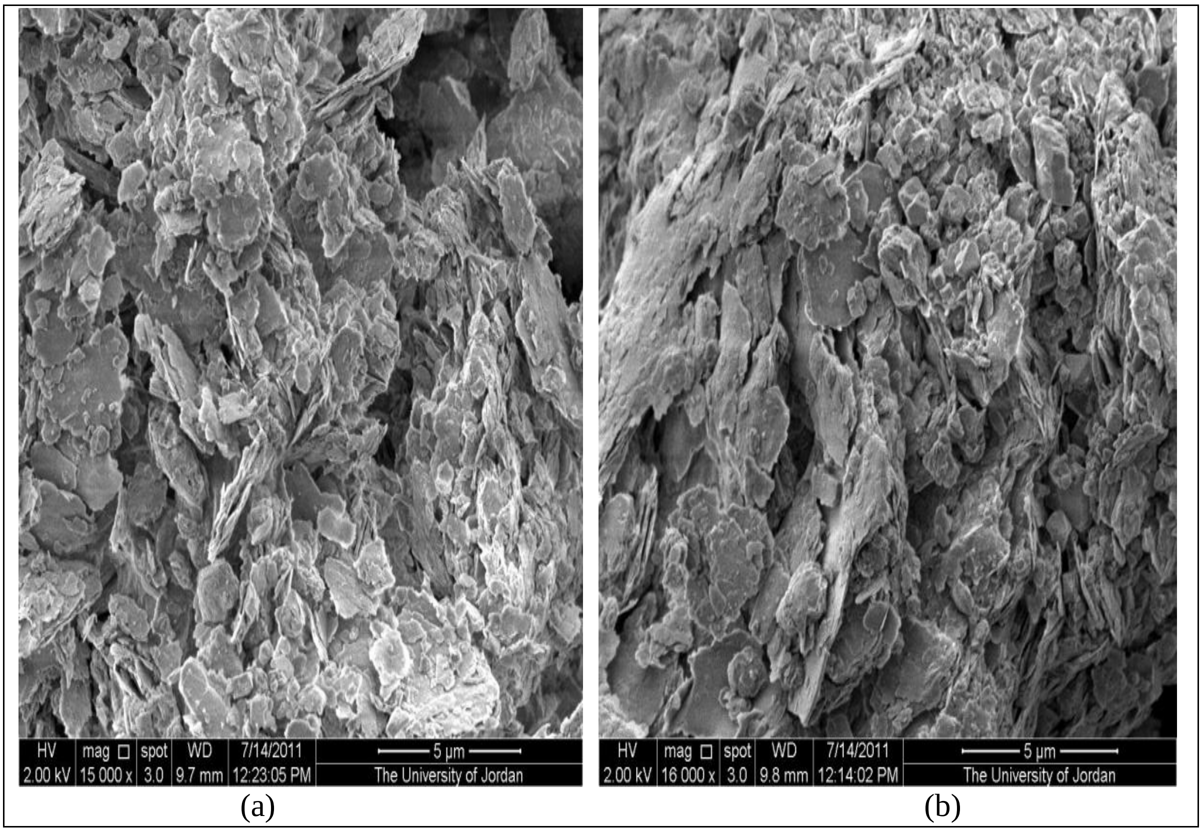


Figure 3.10. SEM micrographs for RK (a) unmodified (b) modified.

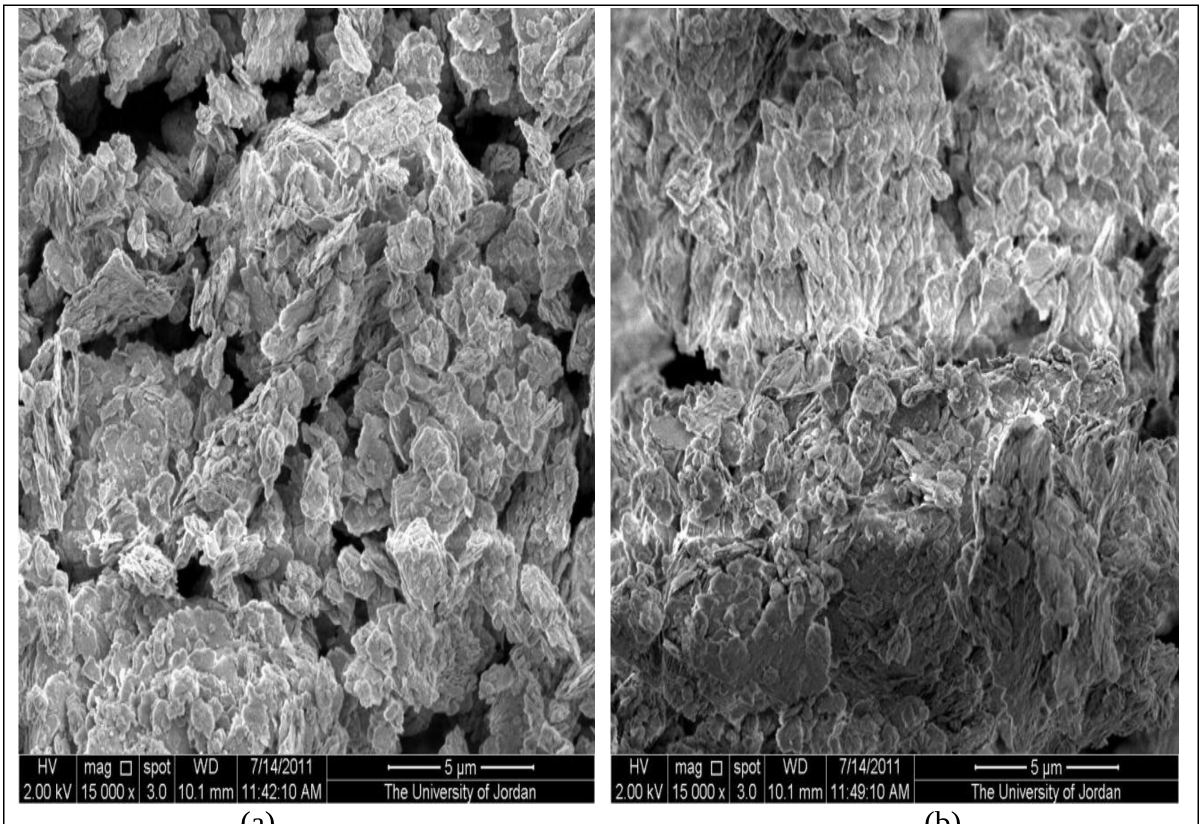


Figure 3.11. SEM micrographs for Ben (a) unmodified (b) modified.

3.6 XRD for unmodified and modified clays

Figure 3.12 shows the X-ray pattern for unmodified and modified white kaolin. The peak at 11.5^{o} was observed in unmodified sample but it disappeared after FH addition. The X-ray pattern for modified sample exhibit red shift by θ=0.3^{o}, this is could be due to the interaction with the FHA as explained in FT-IR results.

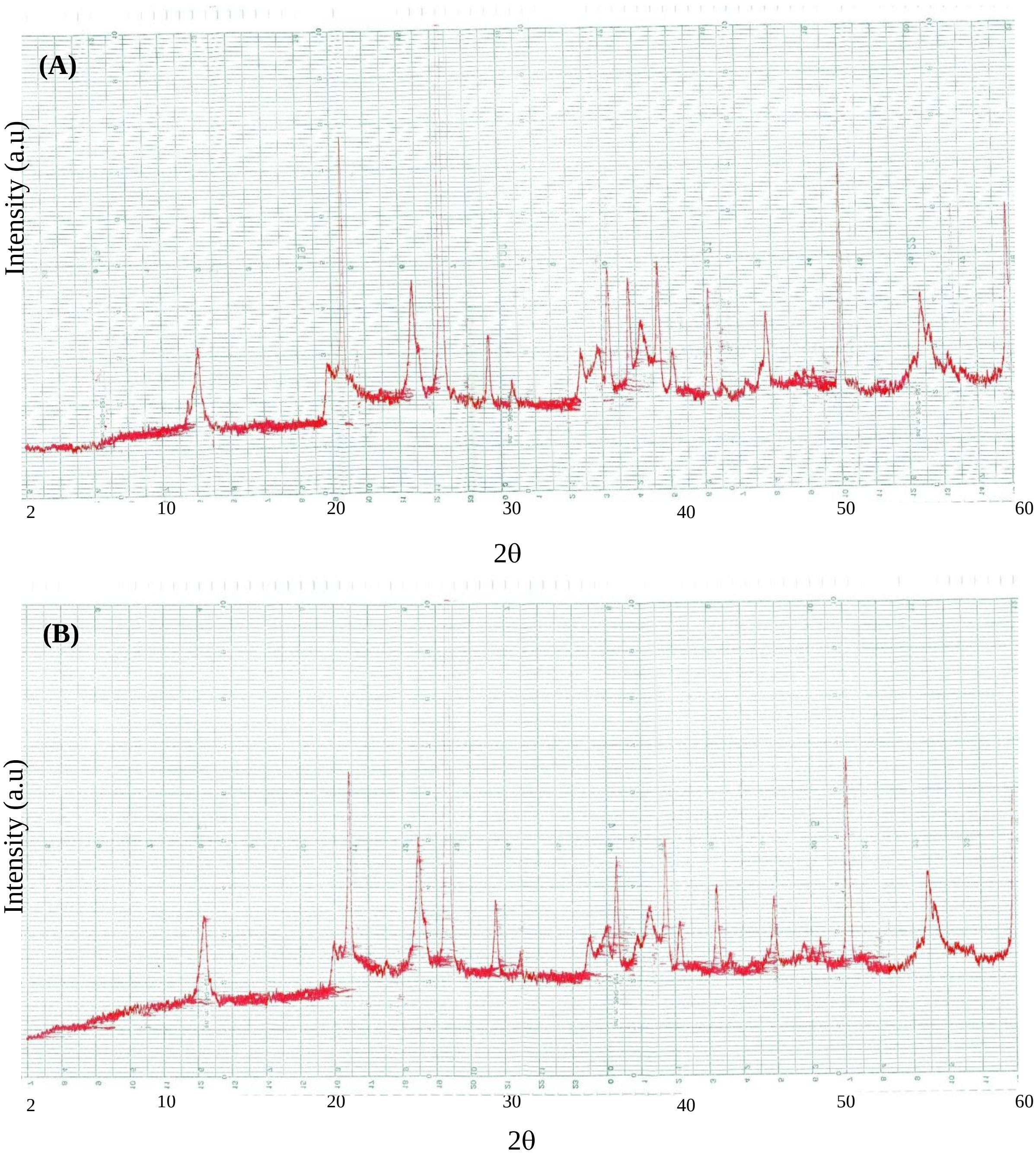


Figure 3.12. X-ray pattern for WK (A) unmodified (B) modified.

Figure 3.13 shows the X-ray pattern for unmodified and modified red kaolin. The peaks at 11.5^o , 29.16 ^{o}, 31.14 ^{o}, 43.6 ^{o} were observed for unmodified are matched with standard ICDD belong to the calcium sulfate hydrate or gypsum (00-001-0385), these peaks were disappeared after FHA modification.

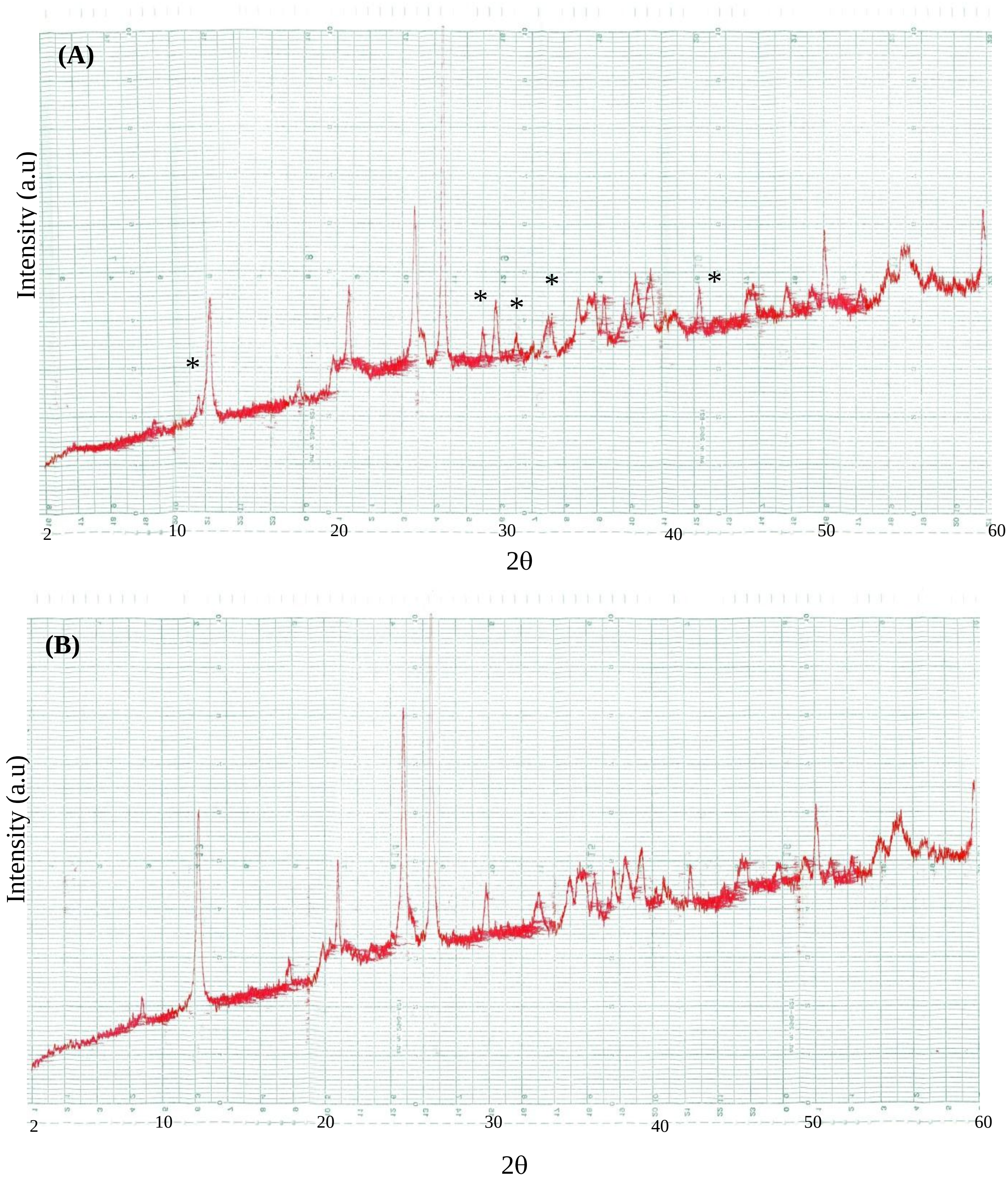


Figure 3.13. X-ray pattern for RK (A) unmodified (B) modified.

Figure 3.14 shows the X-ray pattern for unmodified and modified bentonite. The peaks at 9.4^o ,12.2^o, 20.5^o, 24.9^o, 36.9^o were observed for unmodified bentonite are matched with standard ICDD belong to the Sodium Aluminum Silicate Hydroxide Hydrate (00-029-1490), no change in the crystal structure for bentonite after modification which could be due to the partial modification by the organic modifier. In addition, the bentonite which consist of quartz (ICDD No.: 00-007-0346) and other mineral have high degree of crystallinity compared with the FHA modifier which led to identical appearance for the X-ray pattern for the bentonite.

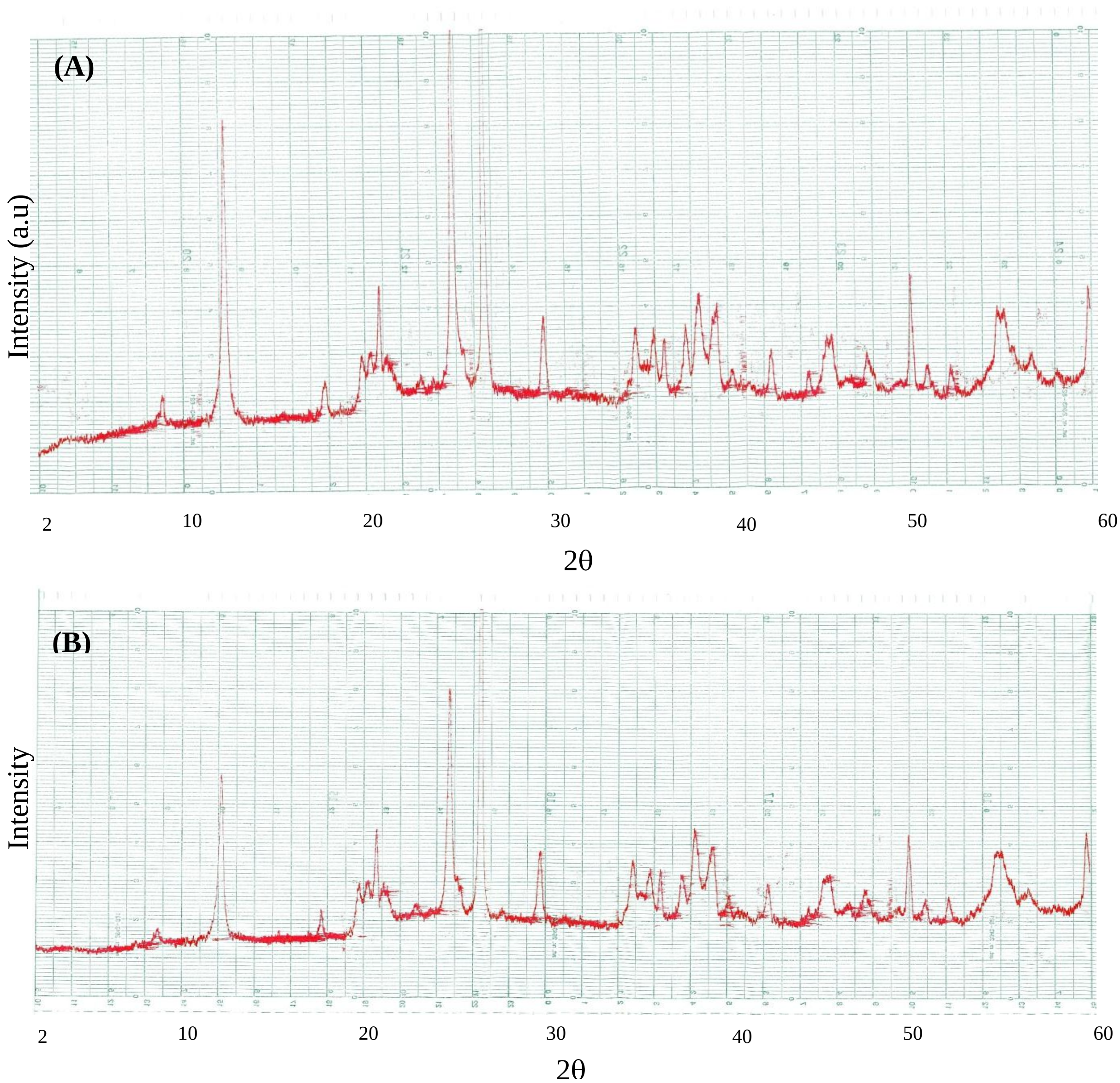


Figure 3.14. X-ray pattern for Ben (A) unmodified (B) modified.

3.7 Mass uptake study

Figures from (3.15-3.55) and the Tables from (3.5-3.45) show that the maximum uptake occurred at 3 h, and about half of FHA/S was uptaken after 1 h, they also show that the mass uptake became nearly constant after 3 h for each type of clay with various types of vegetable oils, and because of the presence of ethanol which is 70 %, some of it evaporated with time, that's why the line was not fixed.

The uptake was calculated by dividing the maximum value after 3 h by the weight of the clay. A comparison between the three types of clays with the same oil showed that in basic medium, the red kaolin had the highest uptake ratio value, then white kaolin and bentonite respectively, but in acidic medium the red kaolin also had the highest uptake ratio value, then bentonite and white kaolin respectively.

In another comparison between all types of the oils with the same type of the clay the uptake mass ratio of FHA/S was the highest from palm oil then soybean, corn, olive, and sunflower, respectively.

From the results the red kaolin had the highest uptake ratio because it contains Fe as impurities, which made a good chelator with FHA/S.

The palm oil had the best uptake ratio because it has more saturated hydrocarbons and also the hydrocarbon chains are short.

Table 3.5. The mass and mass uptake by WK (1.0538 g) with corn FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.729	0.5139	0.0000
1	0.659	0.4580	0.0559
3	0.603	0.4140	0.0999
6	0.606	0.4163	0.0976
12	0.611	0.4203	0.0936
18	0.615	0.4234	0.0905
24	0.62	0.4273	0.0866
48	0.636	0.4399	0.0740

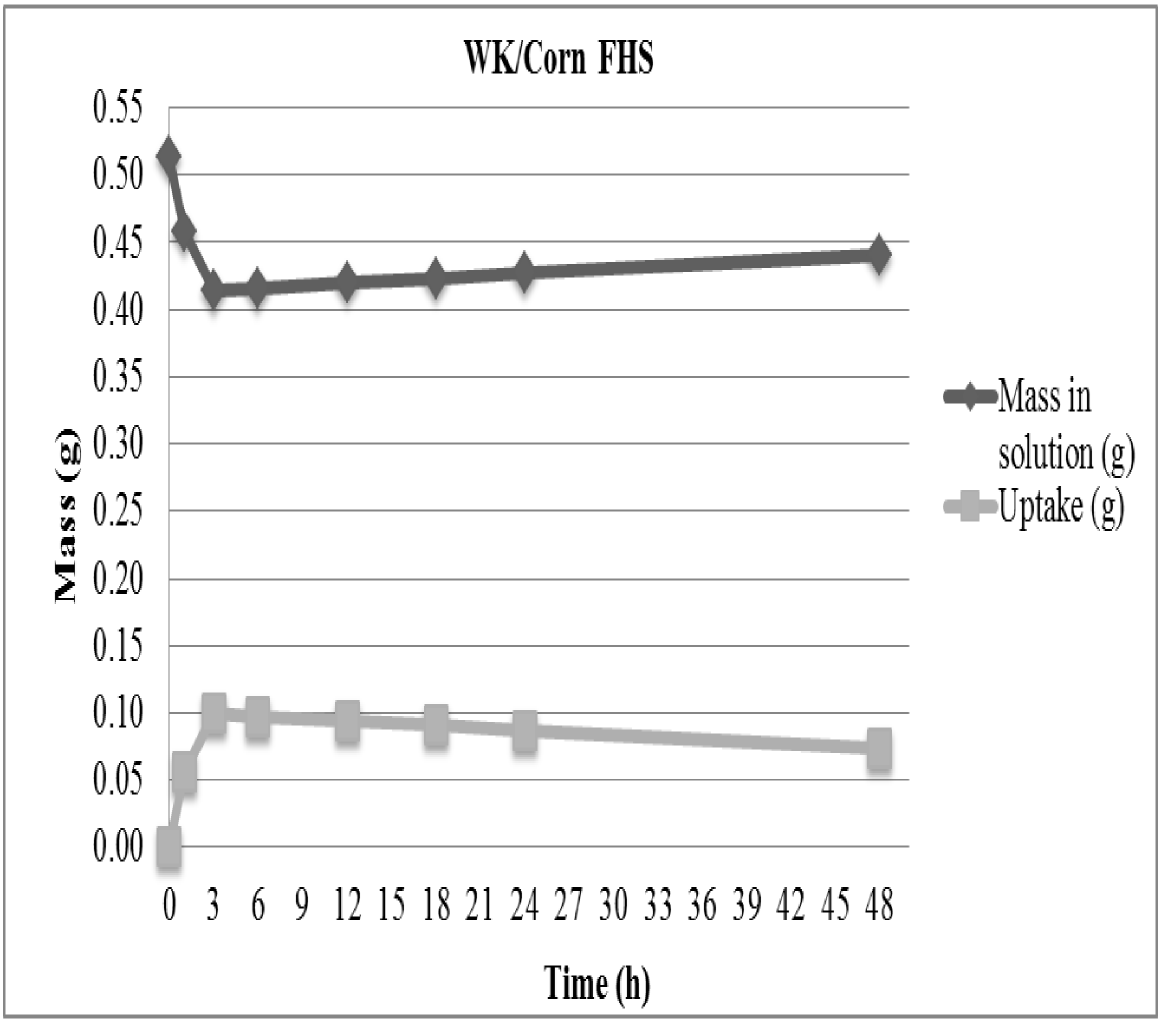


Figure 3.15. Mass uptake of FHS from corn oil by WK with time.

Table 3.6. The mass and mass uptake by WK (1.0129 g) with corn FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.724	0.5094	0.0000
1	0.442	0.2875	0.2219
3	0.244	0.1320	0.3774
6	0.248	0.1351	0.3743
12	0.253	0.1390	0.3704
18	0.257	0.1422	0.3672
24	0.262	0.1461	0.3633
48	0.28	0.1603	0.3491

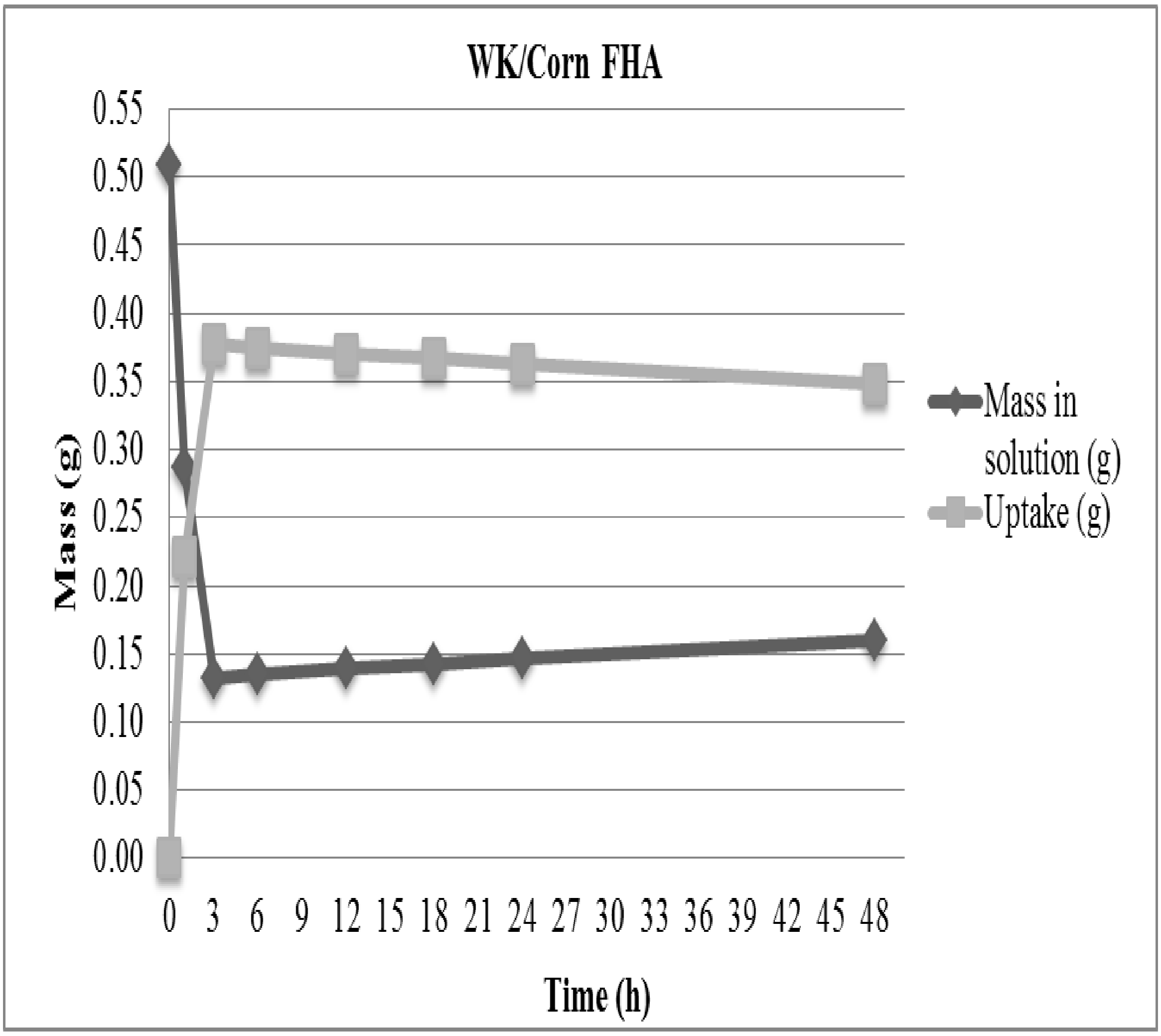


Figure 3.16. Mass uptake of FHA from corn oil by WK with time.

Table 3.7. The mass and mass uptake by RK (1.0819 g) with corn FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.73	0.5142	0.0000
1	0.635	0.4391	0.0751
3	0.559	0.3794	0.1348
6	0.563	0.3826	0.1316
12	0.568	0.3865	0.1277
18	0.572	0.3896	0.1246
24	0.576	0.3928	0.1214
48	0.595	0.4077	0.1065

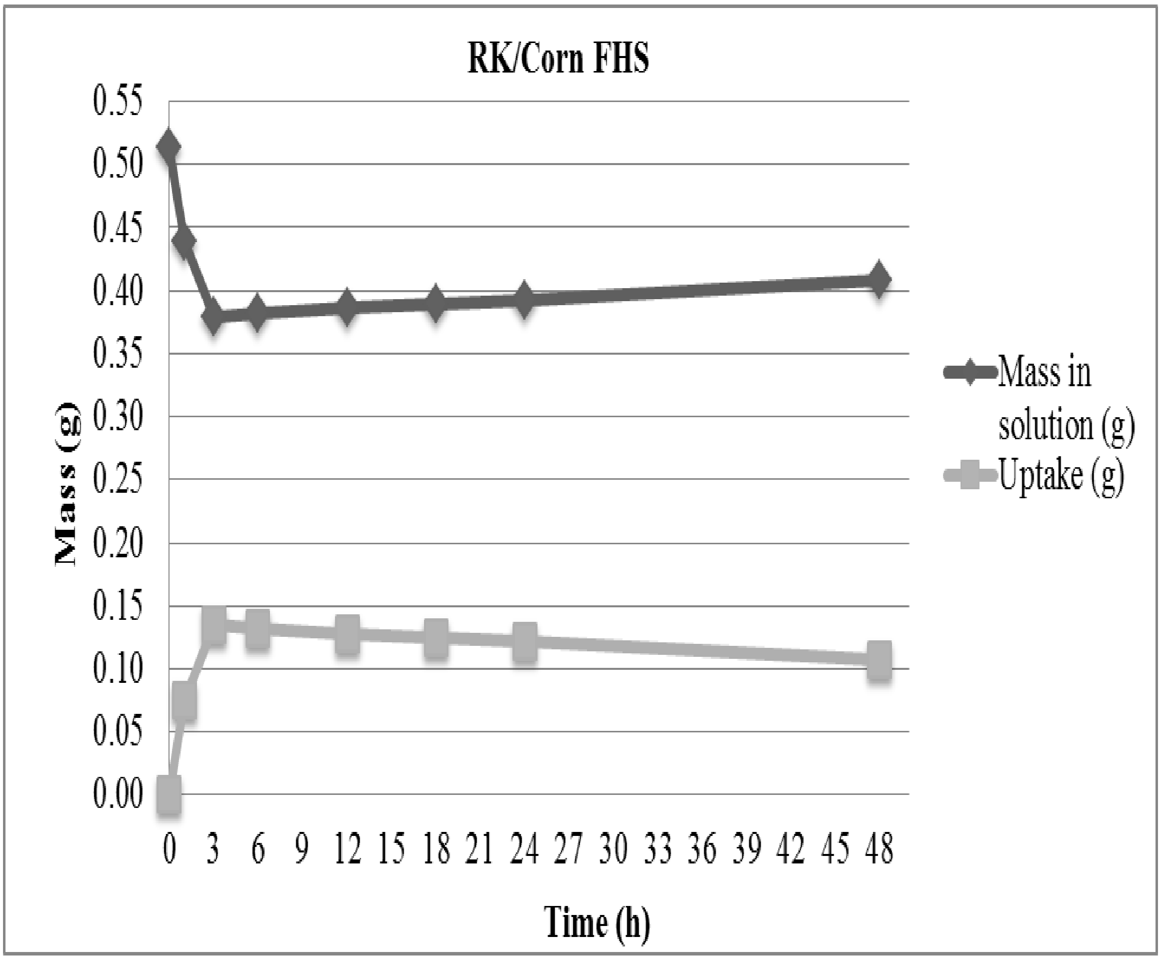


Figure 3.17. Mass uptake of FHS from corn oil by RK with time.

Table 3.8. The mass and mass uptake by RK (1.0517 g) with corn FHA

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.736	0.5183	0.0000
1	0.366	0.2278	0.2905
3	0.182	0.0833	0.4350
6	0.185	0.0856	0.4327
12	0.189	0.0888	0.4295
18	0.193	0.0919	0.4264
24	0.198	0.0958	0.4225
48	0.215	0.1092	0.4091

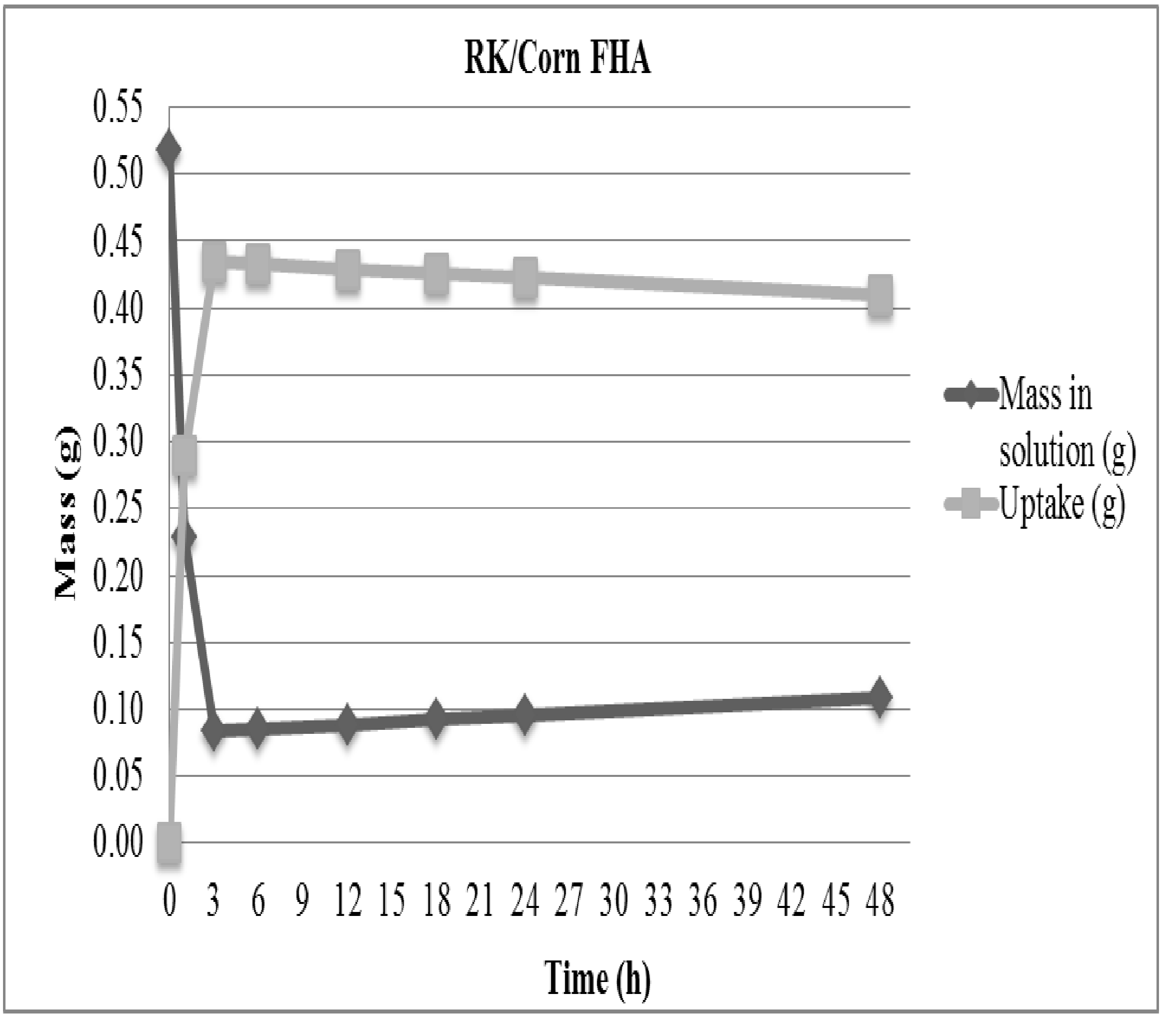


Figure 3.18. Mass uptake of FHA from corn oil by RK with time.

Table 3.9. The mass and mass uptake by Ben (0.9326 g) with corn FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.748	0.5269	0.0000
1	0.71	0.4980	0.0289
3	0.664	0.4619	0.065
6	0.667	0.4643	0.0626
12	0.671	0.4674	0.0595
18	0.676	0.4713	0.0556
24	0.681	0.4753	0.0516
48	0.696	0.4870	0.0399

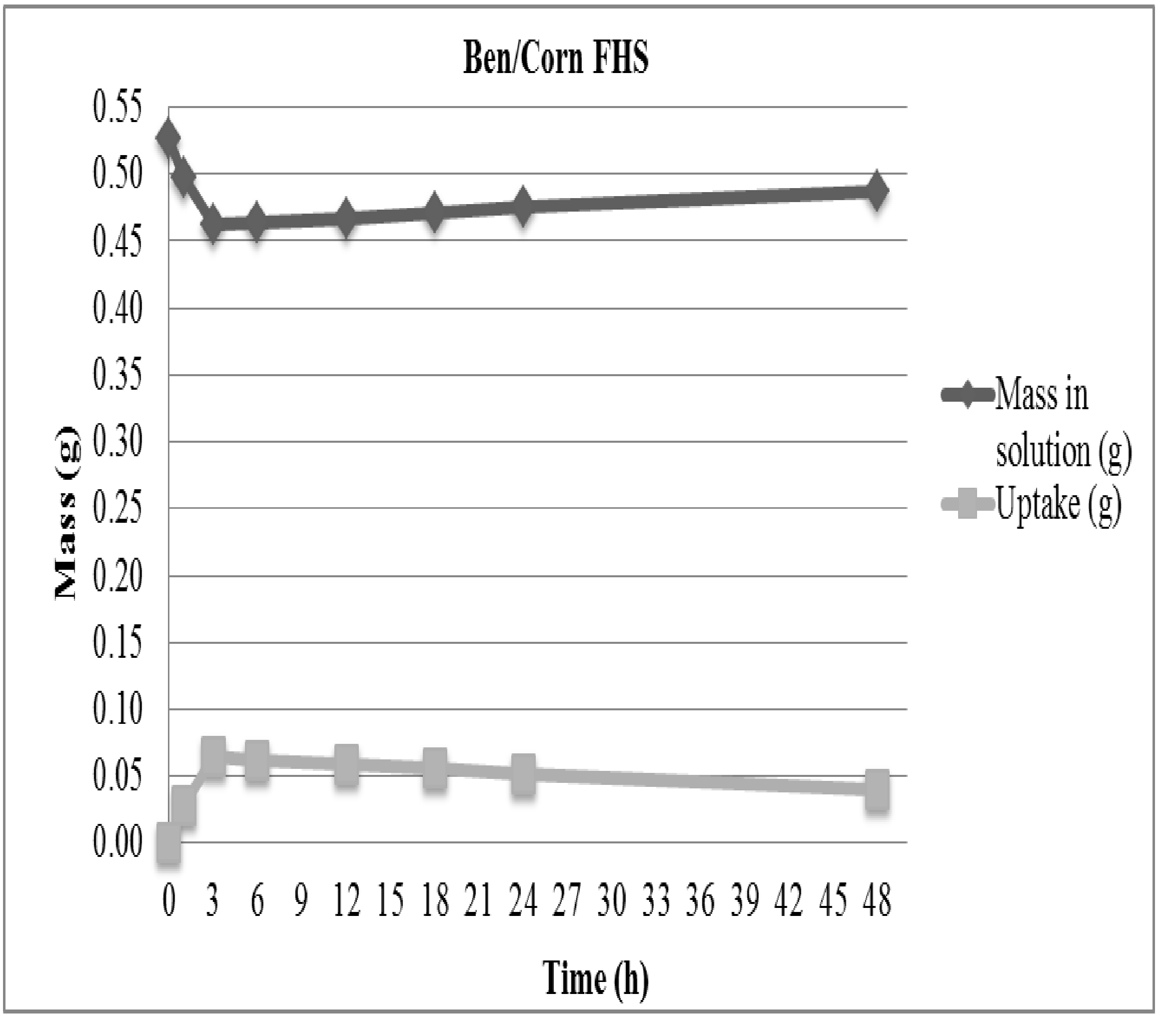


Figure 3.19. Mass uptake of FHS from corn oil by Ben with time.

Table 3.10. The mass and mass uptake by Ben (1.0030 g) with corn FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.725	0.5097	0.0000
1	0.399	0.2537	0.2560
3	0.206	0.1021	0.4076
6	0.209	0.1045	0.4052
12	0.213	0.1076	0.4021
18	0.217	0.1108	0.3989
24	0.222	0.1147	0.3950
48	0.239	0.1280	0.3817

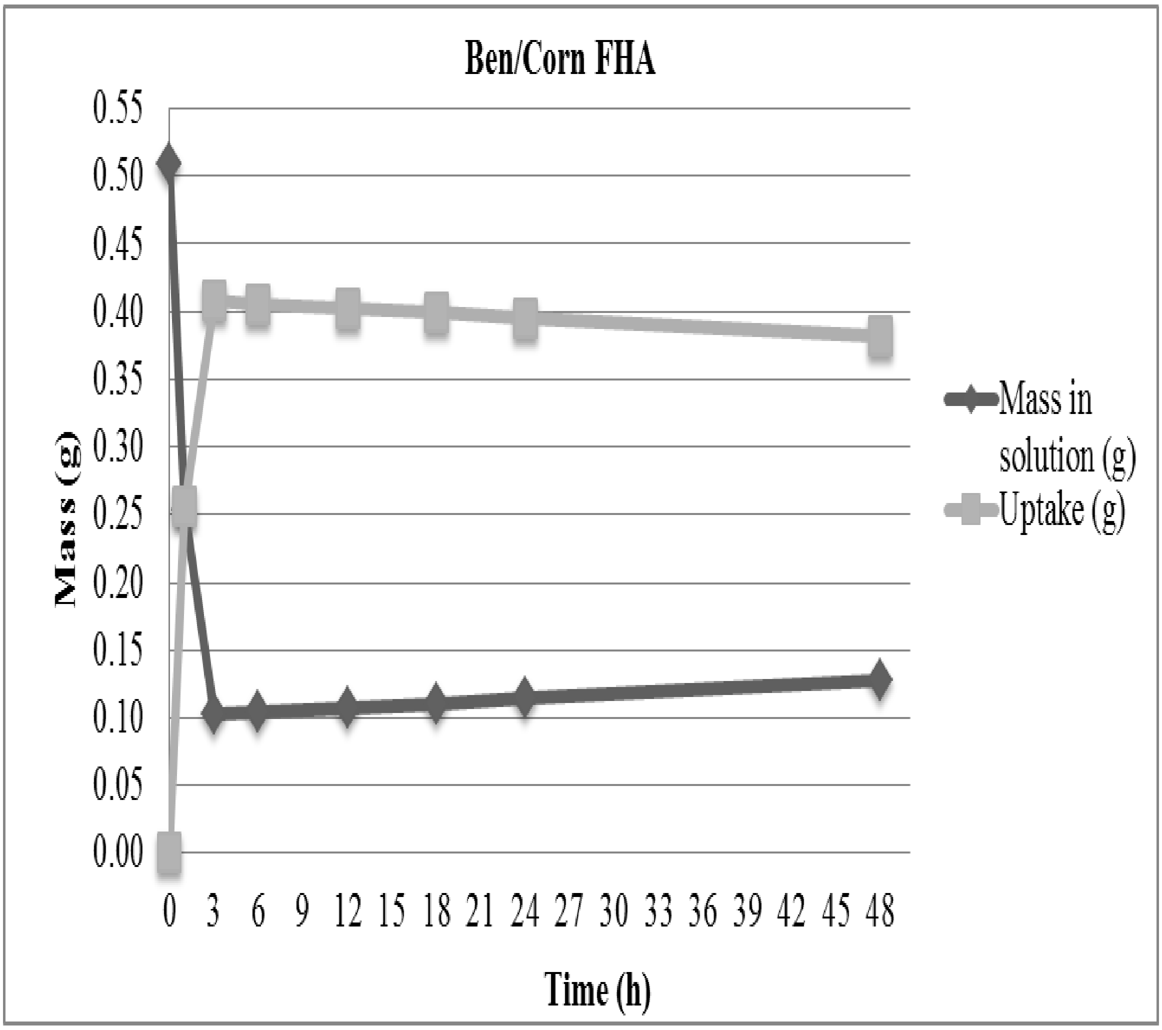


Figure 3.20. Mass uptake of FHA from corn oil by Ben with time.

Table 3.11. The mass and mass uptake by WK (1.6289 g) with olive FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.754	0.5325	0.0000
1	0.658	0.4572	0.0753
3	0.56	0.3802	0.1523
6	0.563	0.3826	0.1499
12	0.566	0.3849	0.1476
18	0.57	0.3881	0.1444
24	0.574	0.3912	0.1413
48	0.59	0.4038	0.1287

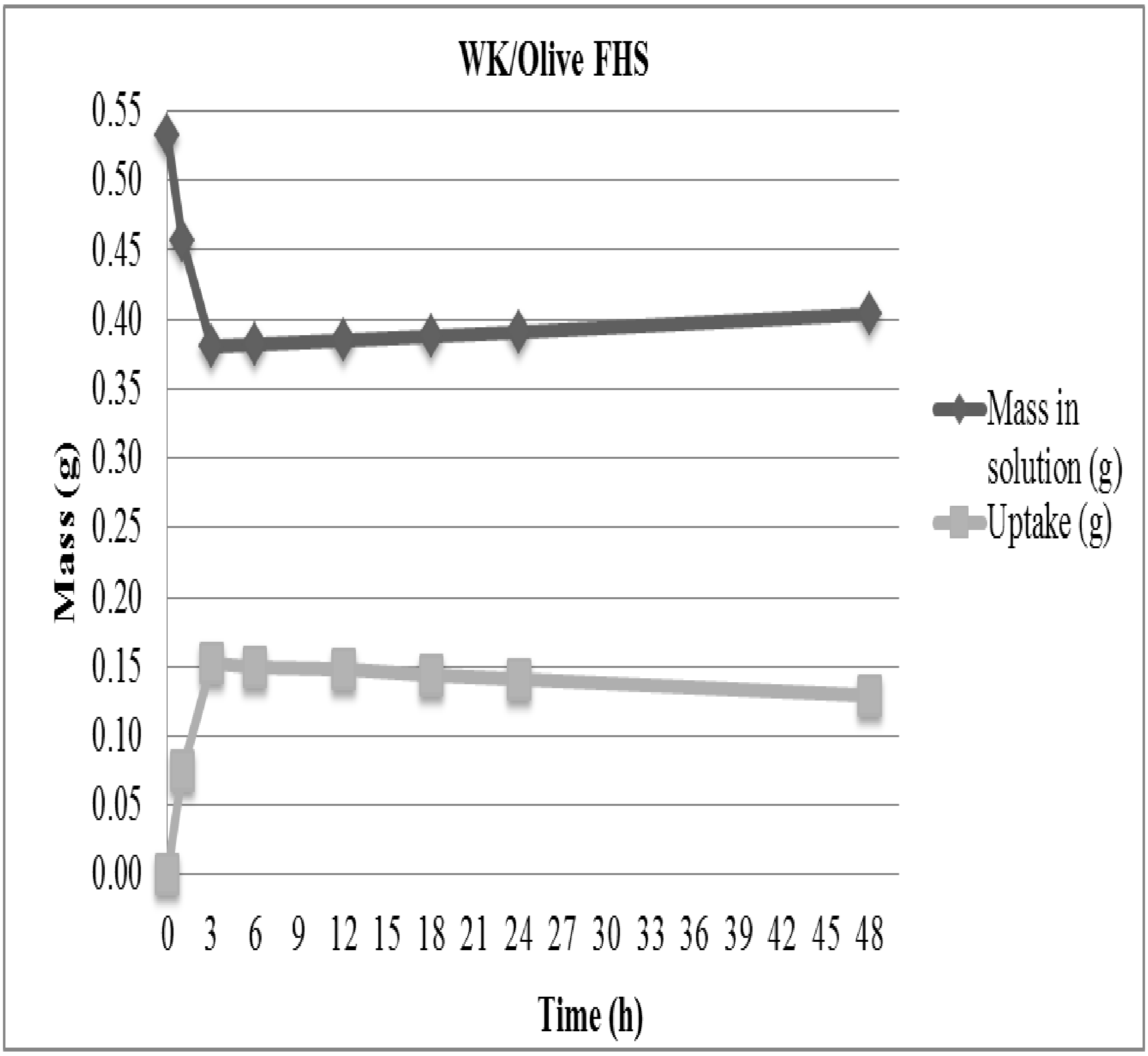


Figure 3.21. Mass uptake of FHS from olive oil by WK with time.

Table 3.12. The mass and mass uptake by WK (1.0401 g) with olive FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.719	0.5053	0.0000
1	0.44	0.2859	0.2194
3	0.241	0.1296	0.3757
6	0.245	0.1328	0.3725
12	0.249	0.1359	0.3694
18	0.254	0.1398	0.3655
24	0.258	0.143	0.3623
48	0.275	0.1563	0.3490

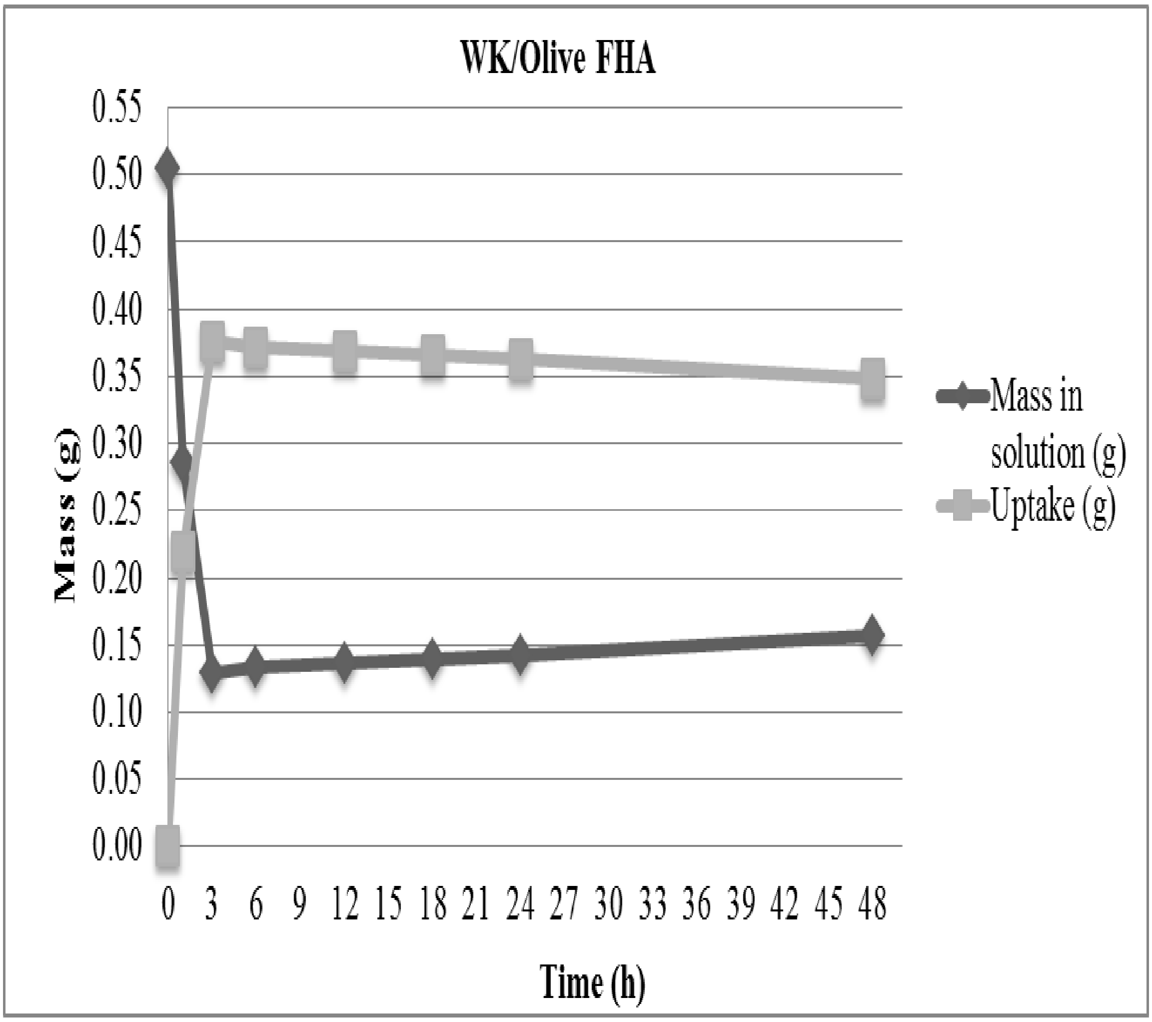


Figure 3.22. Mass uptake of FHA from olive oil by WK with time.

Table 3.13. The mass and mass uptake by red kaolin (1.2180g) with Olive FHS

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.751	0.5301	0.0000
1	0.643	0.4454	0.0847
3	0.568	0.3865	0.1436
6	0.571	0.3888	0.1413
12	0.575	0.392	0.1381
18	0.579	0.3951	0.1350
24	0.584	0.3991	0.1310
48	0.601	0.4124	0.1177

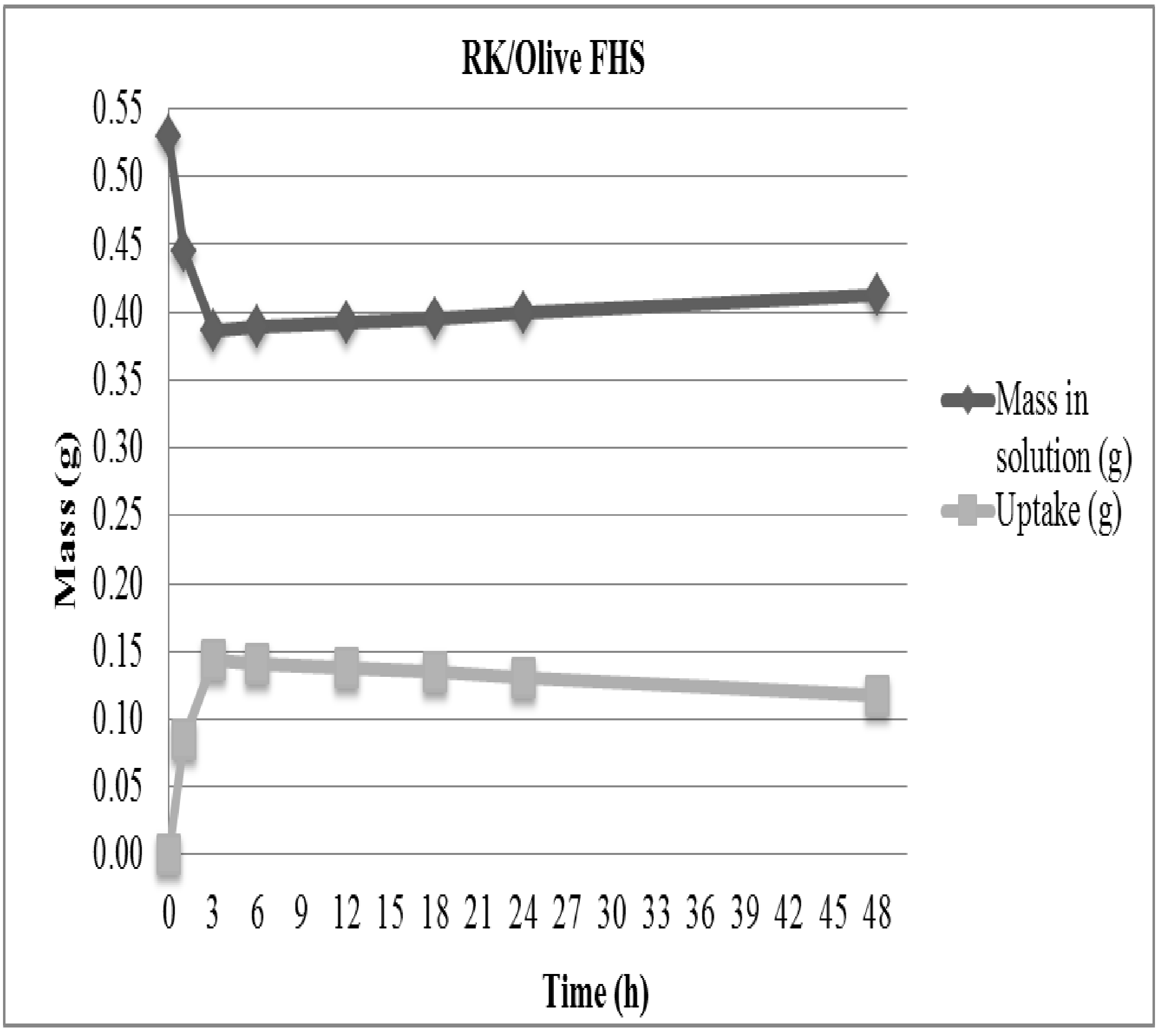


Figure 3.23. Mass uptake of FHS from olive oil by RK with time.

Table 3.14. The mass and mass uptake by RK (1.0838 g) with olive FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.738	0.5210	0.0000
1	0.362	0.2247	0.2963
3	0.178	0.0801	0.4409
6	0.181	0.0825	0.4385
12	0.185	0.0856	0.4354
18	0.19	0.0896	0.4314
24	0.195	0.0935	0.4275
48	0.213	0.1076	0.4134

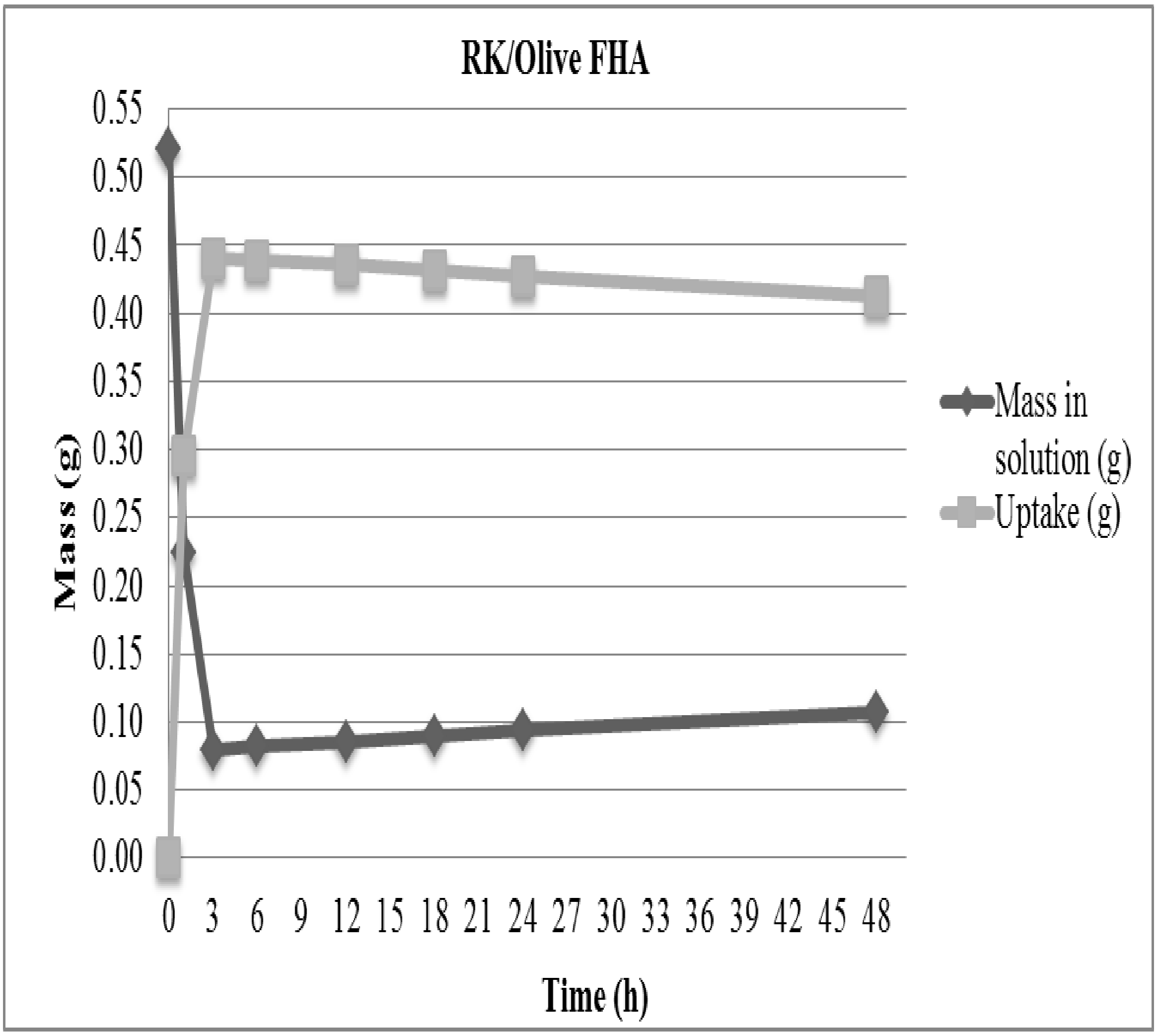


Figure 3.24. Mass uptake of FHA from olive oil by RK with time.

Table 3.15. The mass and mass uptake by Ben (1.0766 g) with olive FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.741	0.5224	0.0000
1	0.693	0.4847	0.0377
3	0.648	0.4493	0.0731
6	0.651	0.4517	0.0707
12	0.655	0.4548	0.0676
18	0.66	0.4588	0.0636
24	0.664	0.4619	0.0605
48	0.681	0.4753	0.0471

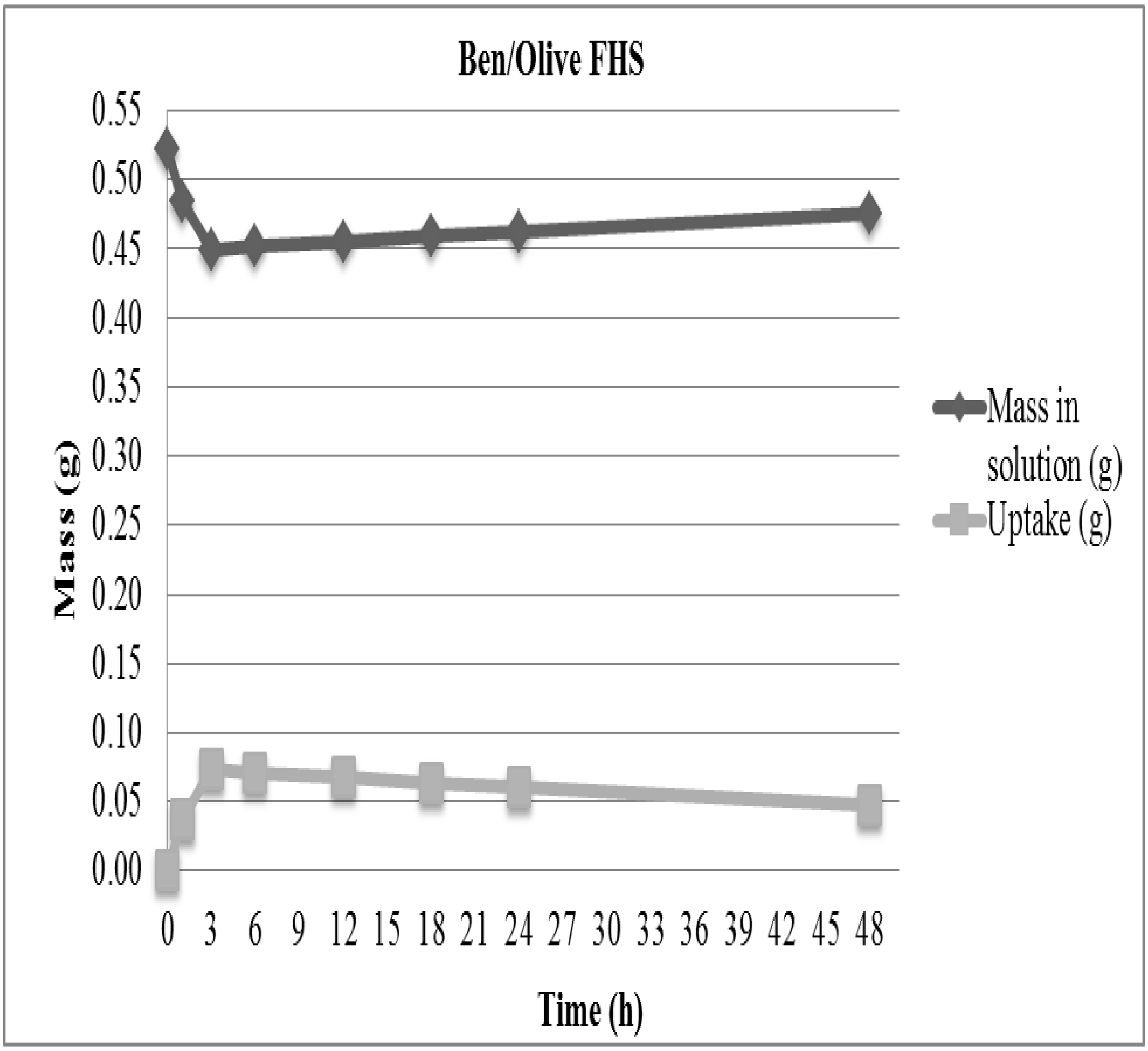


Figure 3.25. Mass uptake of FHS from olive oil by Ben with time.

Table 3.16. The mass and mass uptake by Ben (1.0523 g) with olive FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.713	0.5021	0.0000
1	0.374	0.2341	0.2680
3	0.18	0.0817	0.4204
6	0.184	0.0848	0.4173
12	0.189	0.0888	0.4133
18	0.193	0.0919	0.4102
24	0.197	0.0951	0.4070
48	0.215	0.1092	0.3929

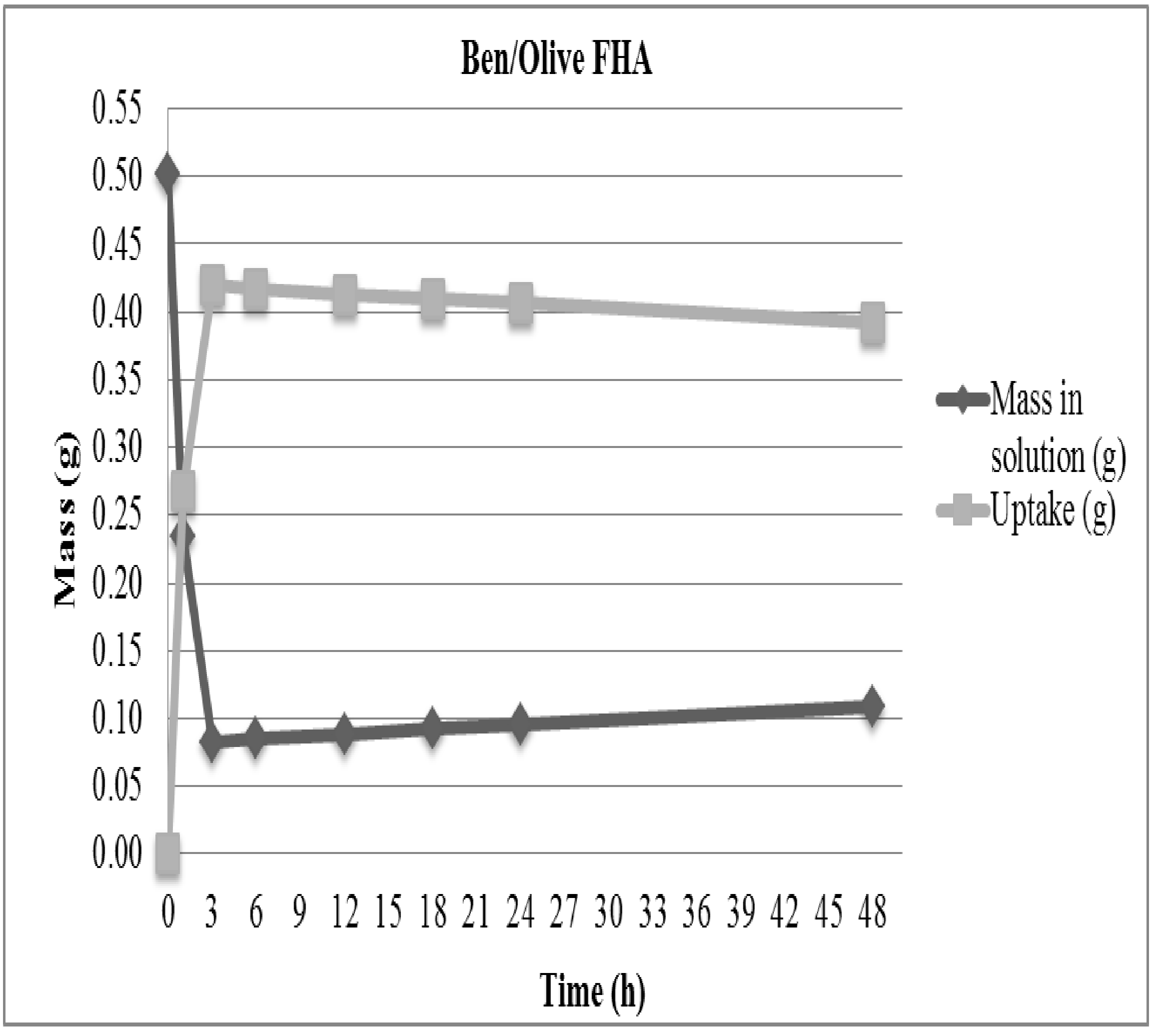


Figure 3.26. Mass uptake of FHA from olive oil by Ben with time.

Table 3.17. The mass and mass uptake by WK (1.0813 g) with palm FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.733	0.5152	0.0000
1	0.656	0.4556	0.0596
3	0.598	0.4101	0.1051
6	0.6	0.4116	0.1036
12	0.603	0.414	0.1012
18	0.607	0.4171	0.0981
24	0.611	0.4203	0.0949
48	0.626	0.4321	0.0831

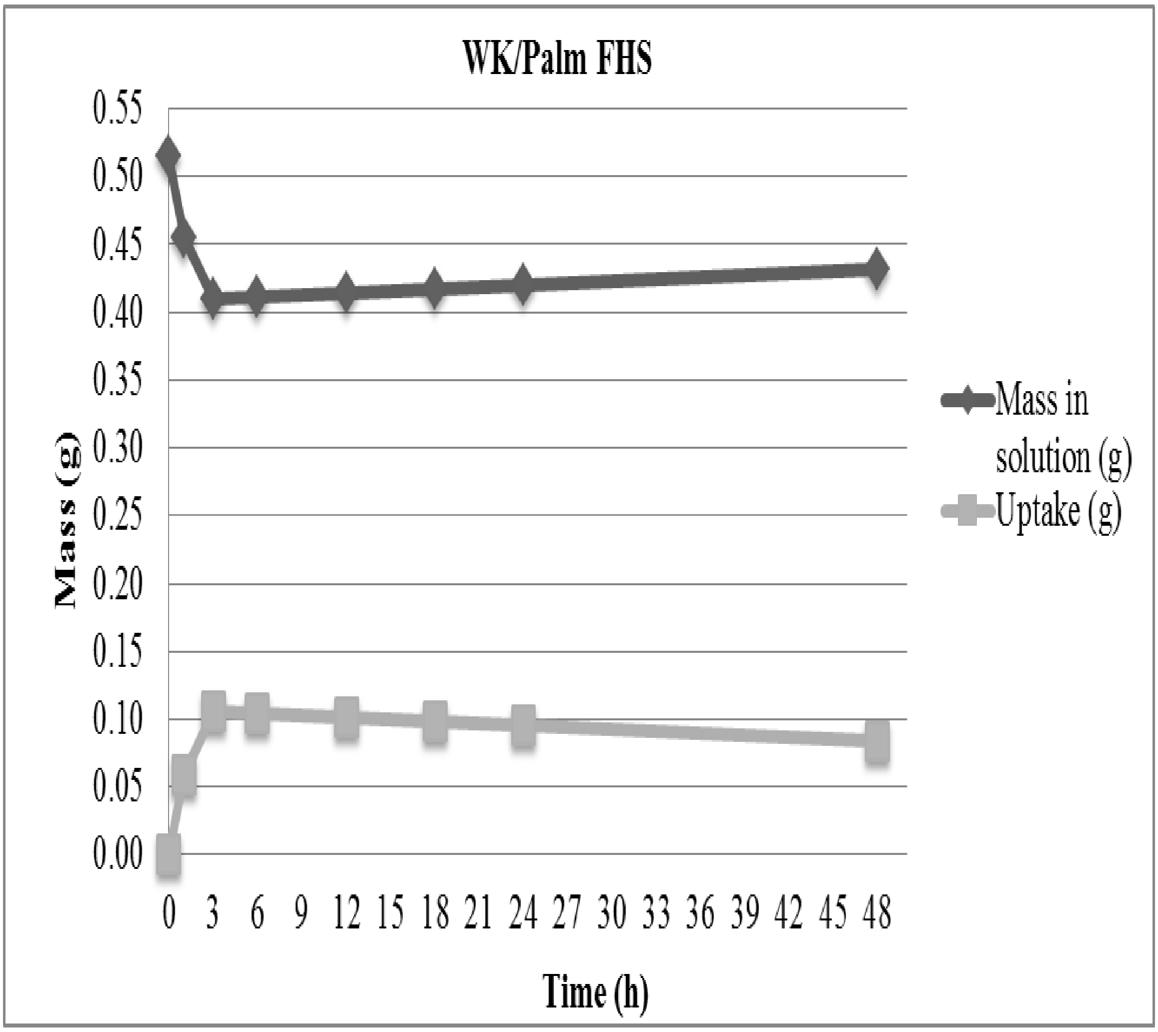


Figure 3.27. Mass uptake of FHS from palm oil by WK with time.

Table 3.18. The mass and mass uptake by WK (1.0200 g) with palm FHA

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.754	0.5343	0.0000
1	0.435	0.2820	0.2523
3	0.236	0.1257	0.4086
6	0.241	0.1296	0.4047
12	0.245	0.1328	0.4015
18	0.249	0.1359	0.3984
24	0.254	0.1398	0.3945
48	0.272	0.1540	0.3803

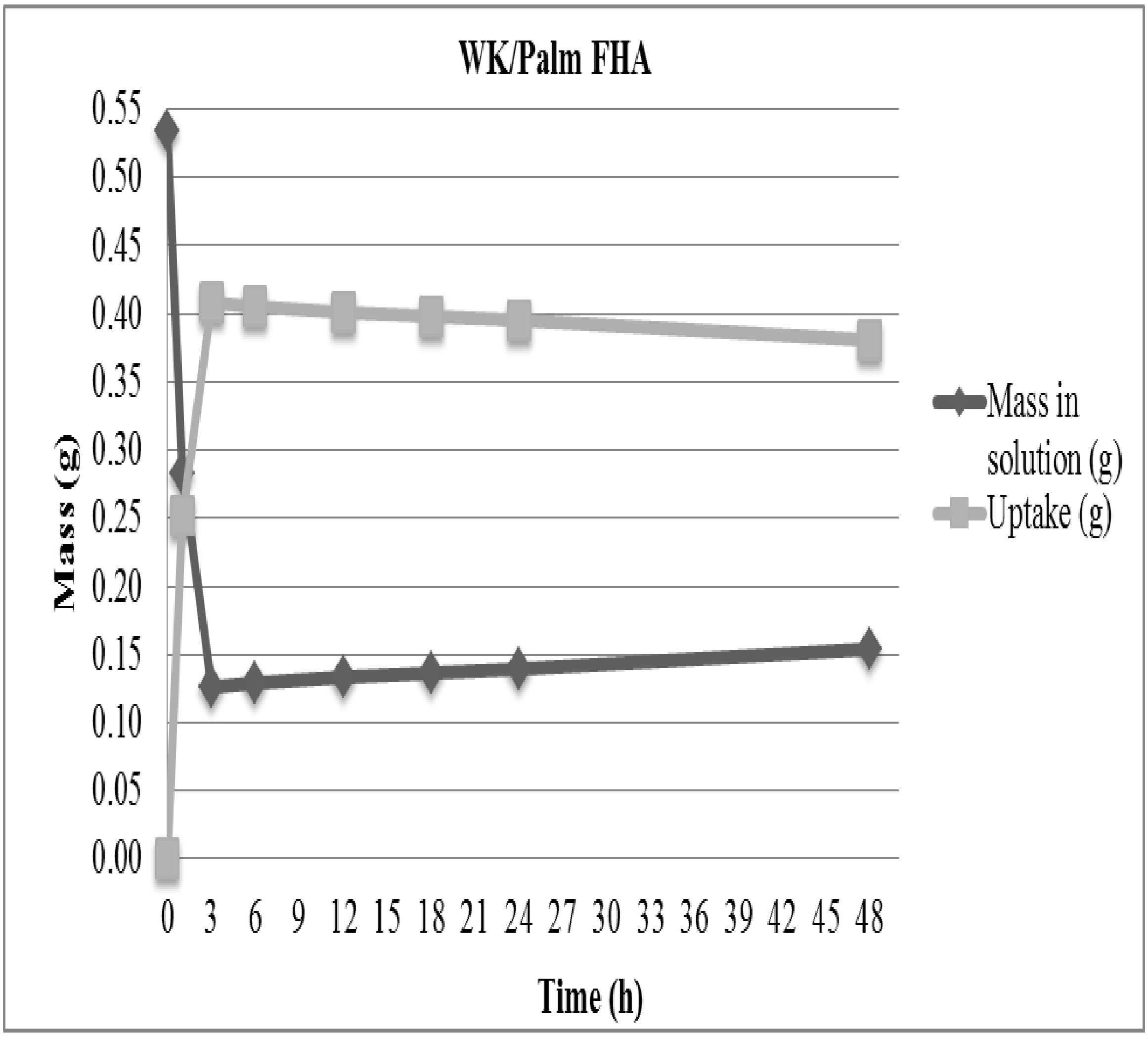


Figure 3.28. Mass uptake of FHA from palm oil by WK with time.

Table 3.19. The mass and mass uptake by RK (1.0380 g) with palm FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.728	0.5140	0.0000
1	0.629	0.4344	0.0796
3	0.553	0.3747	0.1393
6	0.556	0.3771	0.1369
12	0.561	0.3810	0.133
18	0.564	0.3833	0.1307
24	0.569	0.3873	0.1267
48	0.586	0.4006	0.1134

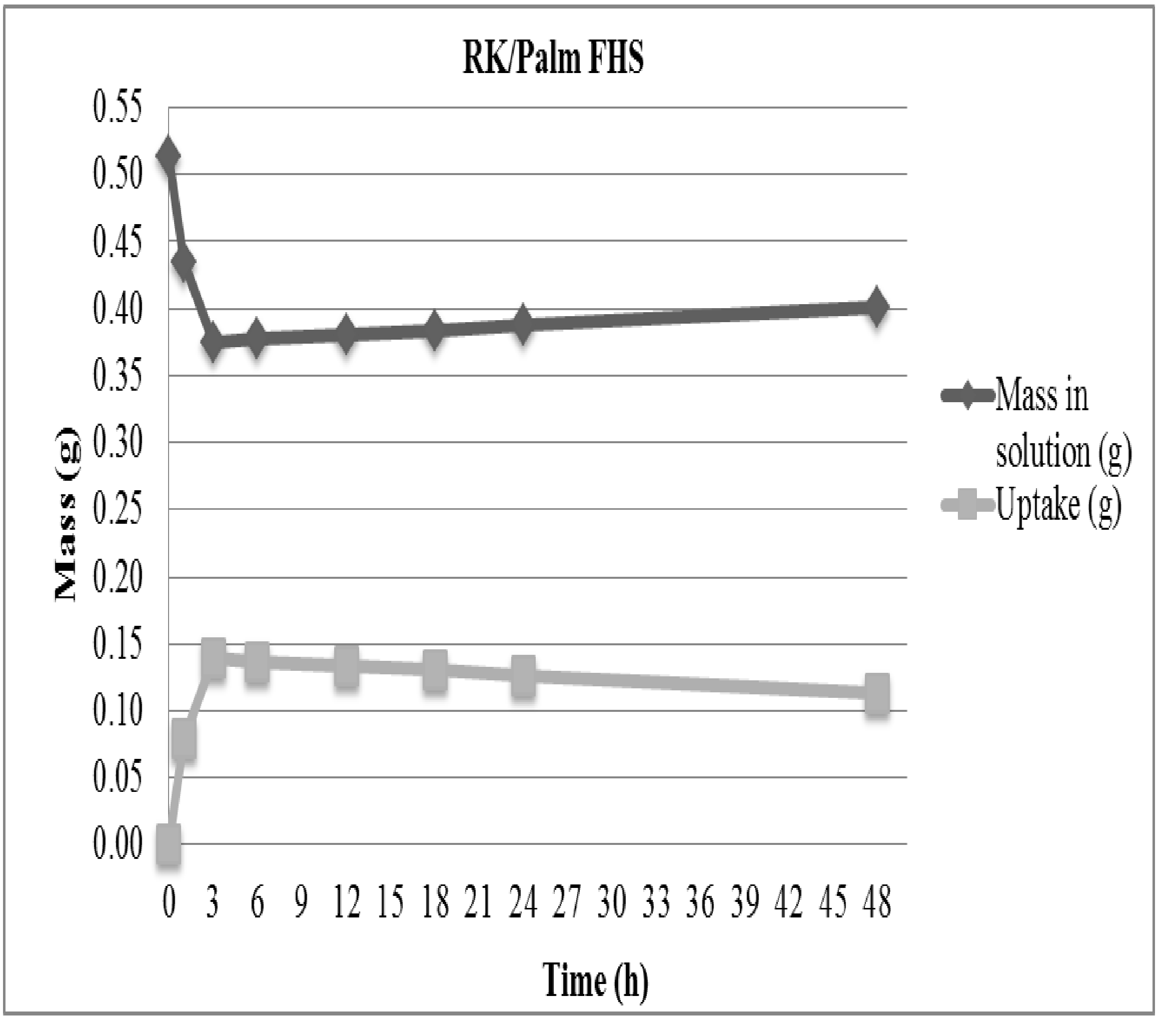


Figure 3.29. Mass uptake of FHS from palm oil by RK with time.

Table 3.20. The mass and mass uptake by RK (1.0207 g) with palm FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.742	0.5250	0.0000
1	0.358	0.2215	0.3035
3	0.174	0.0770	0.4480
6	0.178	0.0801	0.4449
12	0.182	0.0833	0.4417
18	0.188	0.0880	0.4370
24	0.192	0.0911	0.4339
48	0.211	0.1060	0.4190

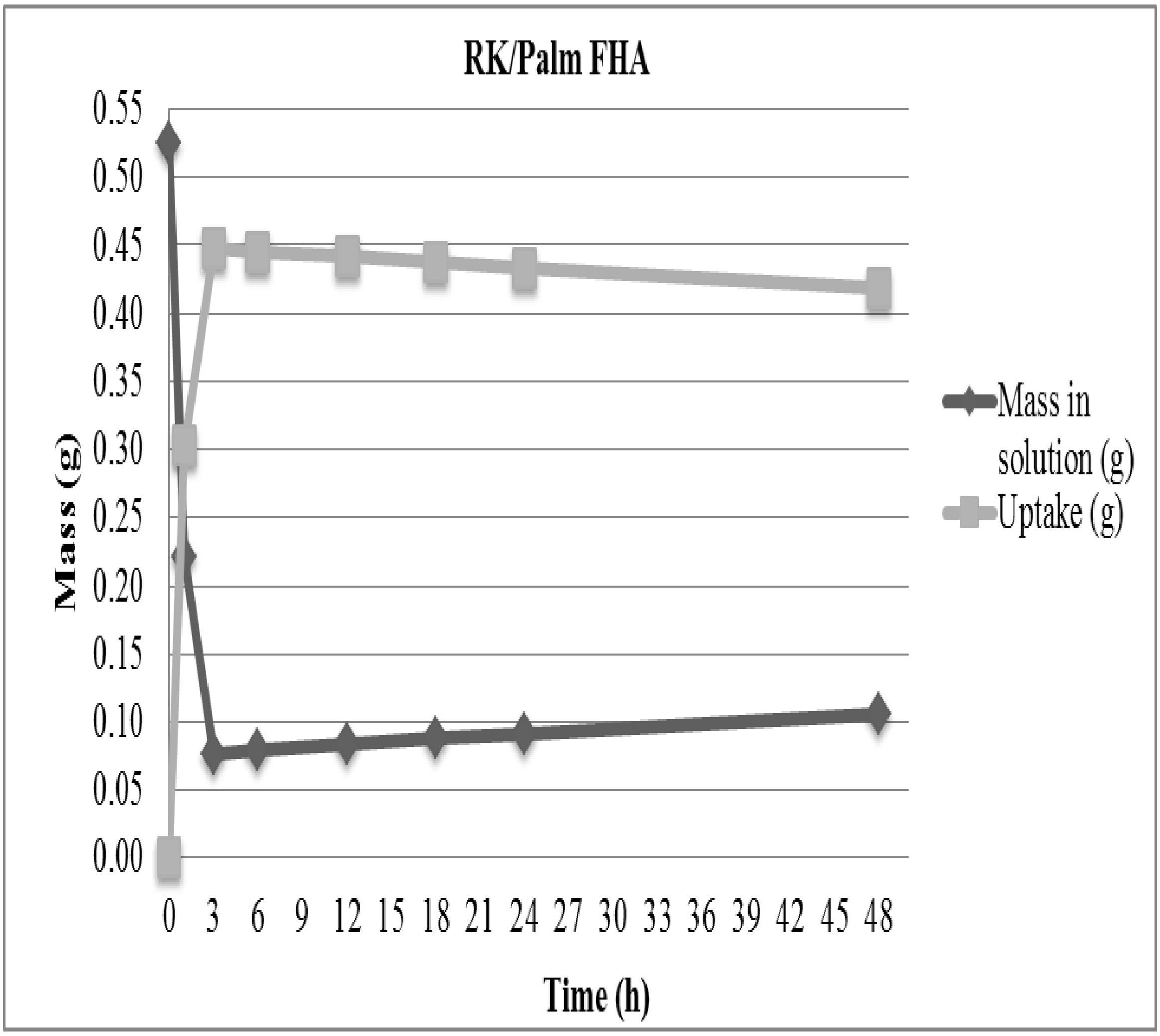


Figure 3.30. Mass uptake of FHA from palm oil by RK with time.

Table 3.21. The mass and mass uptake by Ben (1.0025 g) with palm FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.752	0.5315	0.0000
1	0.698	0.4886	0.0429
3	0.652	0.4525	0.079
6	0.655	0.4548	0.0767
12	0.659	0.458	0.0735
18	0.664	0.4619	0.0696
24	0.669	0.4658	0.0657
48	0.687	0.4800	0.0515

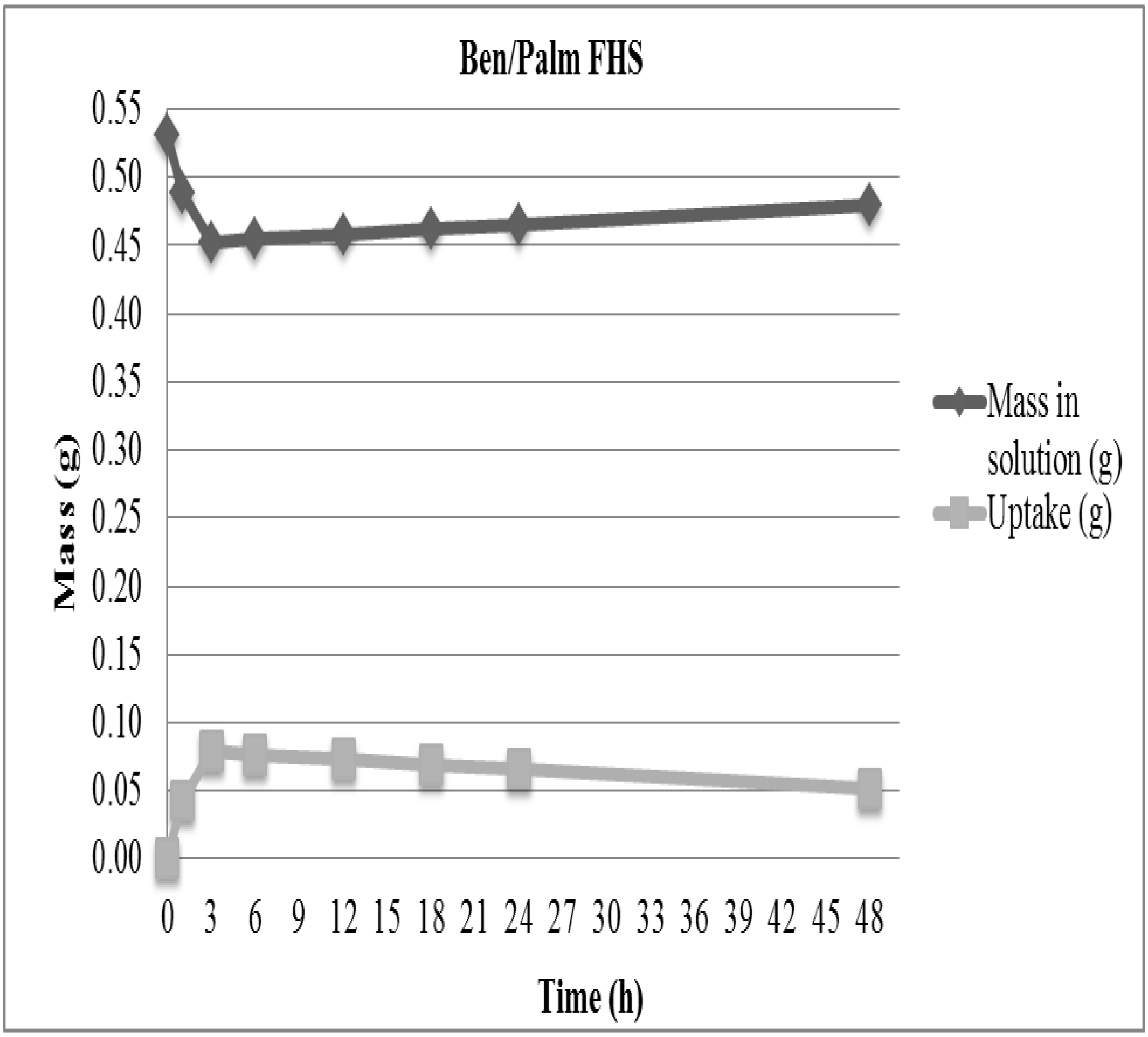


Figure 3.31. Mass uptake of FHS from palm oil by Ben with time.

Table 3.22. The mass and mass uptake by Ben (0.9924 g) with palm FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.715	0.5017	0.0000
1	0.376	0.2357	0.266
3	0.183	0.0841	0.4176
6	0.186	0.0864	0.4153
12	0.19	0.0896	0.4121
18	0.194	0.0927	0.409
24	0.199	0.0966	0.4051
48	0.216	0.1100	0.3917

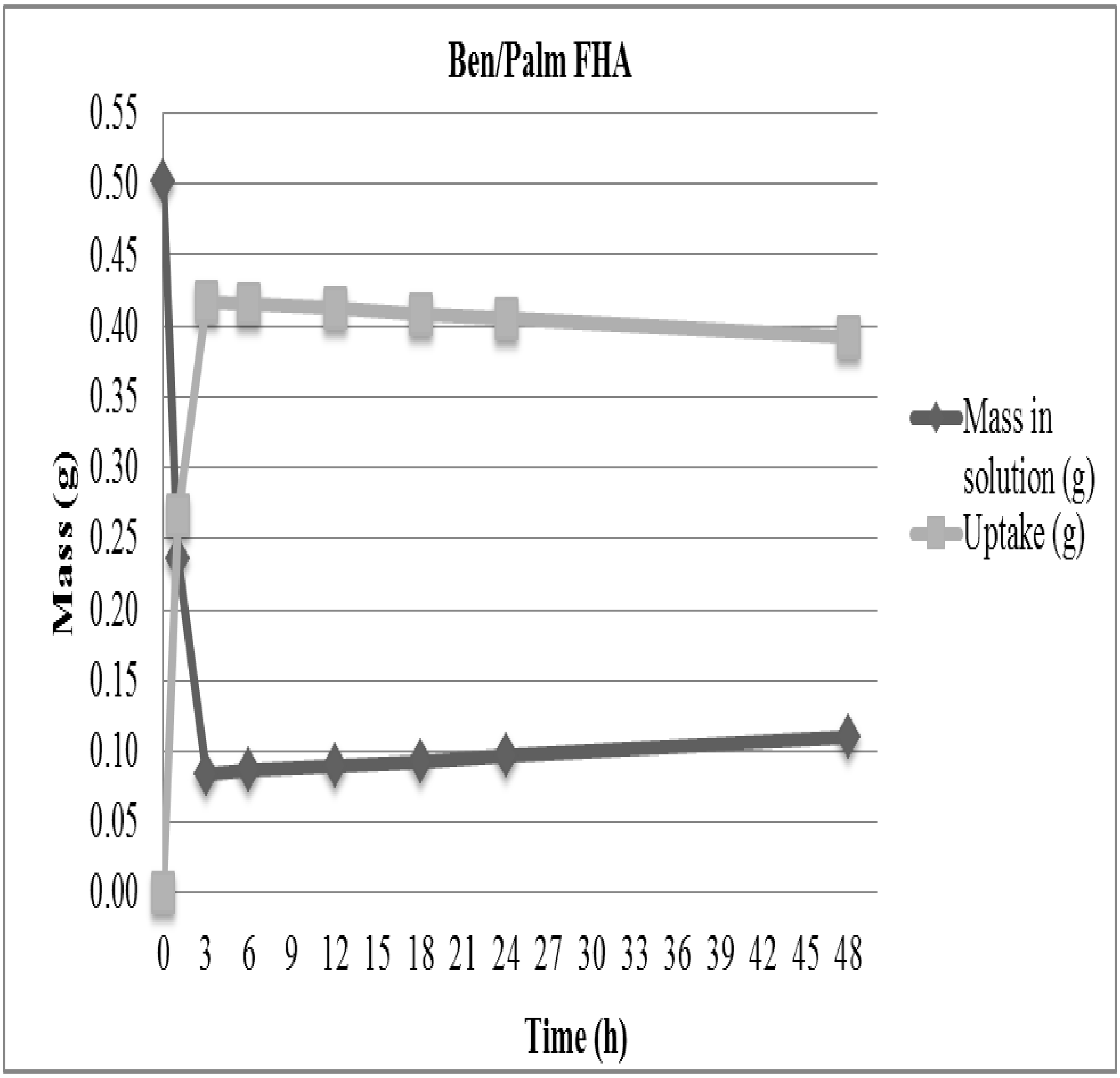


Figure 3.32. Mass uptake of FHA from palm oil by Ben with time.

Table 3.23. The mass and mass uptake by WK (1.3054 g) with soybean FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.725	0.5109	0.0000
1	0.646	0.4478	0.0631
3	0.568	0.3865	0.1244
6	0.571	0.3888	0.1221
12	0.575	0.3920	0.1189
18	0.579	0.3951	0.1158
24	0.583	0.3983	0.1126
48	0.599	0.4108	0.1001

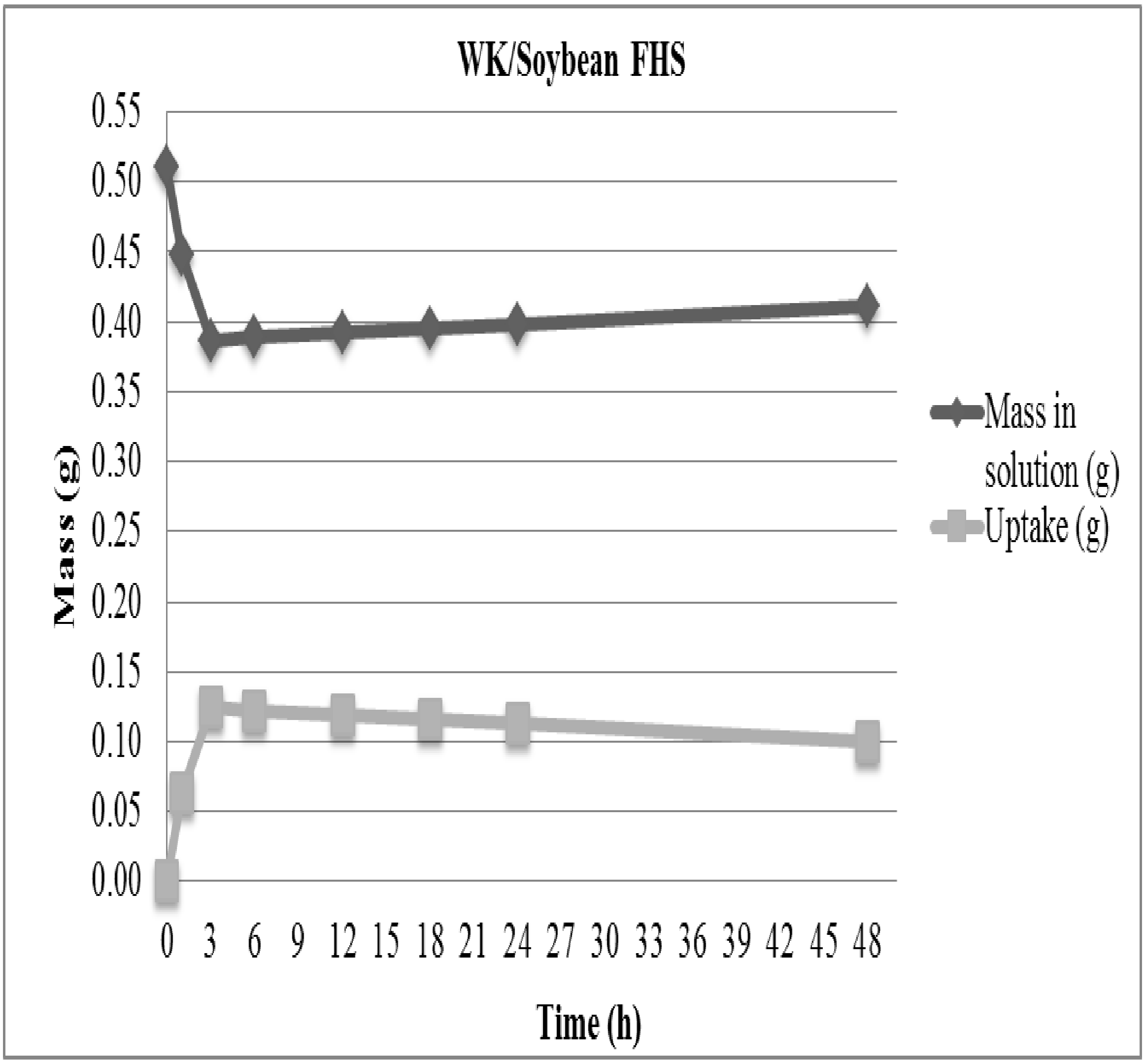


Figure 3.33. Mass uptake of FHS from soybean oil by WK with time.

Table 3.24. The mass and mass uptake by WK (0.9447 g) with soybean FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.723	0.5097	0.0000
1	0.46	0.3016	0.2081
3	0.262	0.1461	0.3636
6	0.266	0.1493	0.3604
12	0.27	0.1524	0.3573
18	0.275	0.1563	0.3534
24	0.279	0.1595	0.3502
48	0.295	0.1720	0.3377

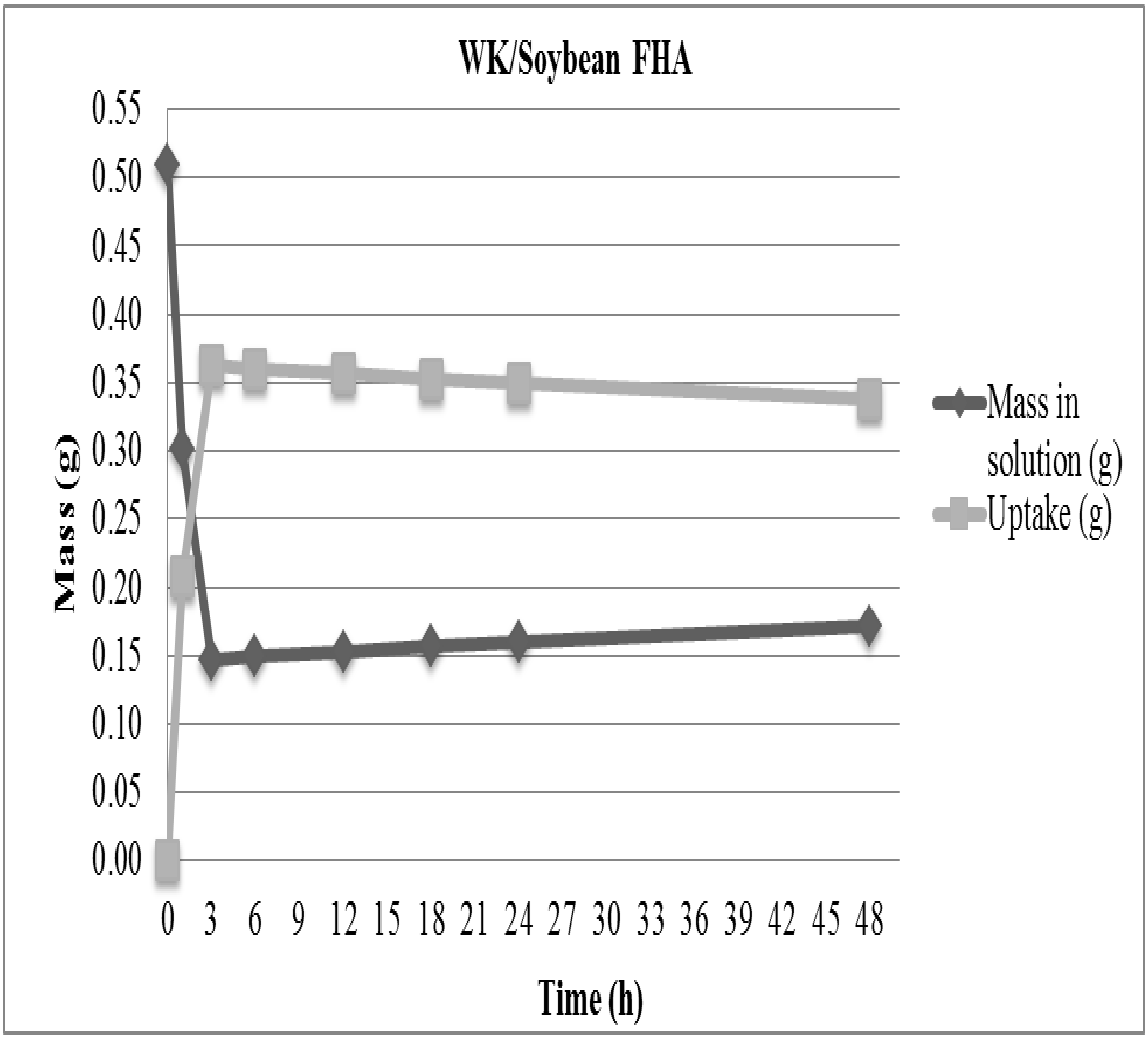


Figure 3.34. Mass uptake of FHA from soybean oil by WK with time.

Table 3.25. The mass and mass uptake by RK (1.1804 g) with soybean FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.753	0.5317	0.0000
1	0.633	0.4375	0.0942
3	0.558	0.3786	0.1531
6	0.561	0.3810	0.1507
12	0.565	0.3841	0.1476
18	0.569	0.3873	0.1444
24	0.574	0.3912	0.1405
48	0.591	0.4046	0.1271

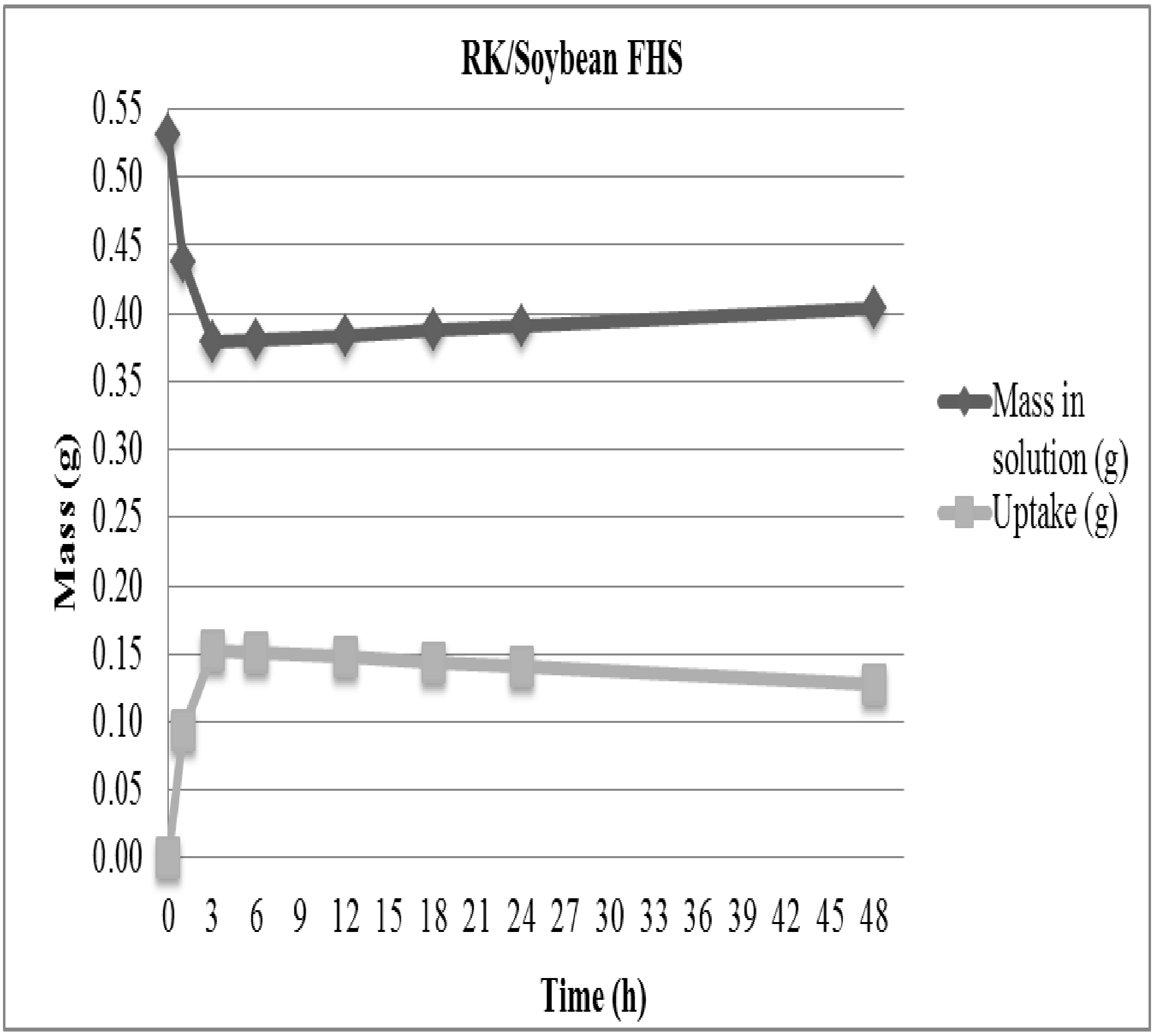


Figure 3.35. Mass uptake of FHS from soybean oil by RK with time.

Table 3.26. The mass and mass uptake by RK (1.0183 g) with soybean FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.723	0.508	0.0000
1	0.36	0.2231	0.2849
3	0.176	0.0786	0.4294
6	0.179	0.0809	0.4271
12	0.183	0.0841	0.4239
18	0.188	0.0880	0.4200
24	0.193	0.0919	0.4161
48	0.211	0.1060	0.4020

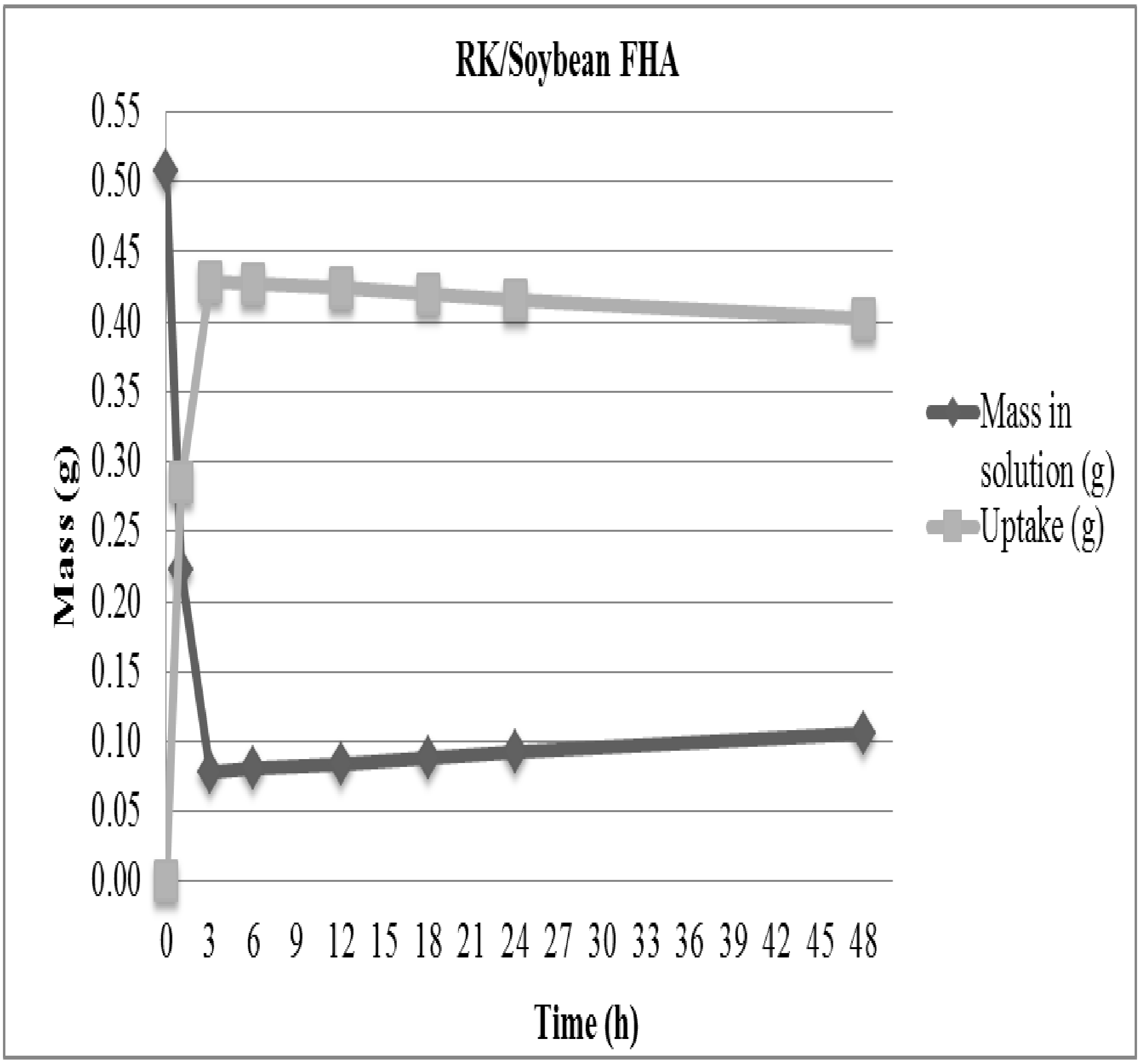


Figure 3.36. Mass uptake of FHA from soybean oil by RK with time.

Table 3.27. The mass and mass uptake by Ben (0.8890 g) with soybean FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.763	0.5401	0.0000
1	0.718	0.5043	0.0358
3	0.682	0.476	0.0641
6	0.685	0.4784	0.0617
12	0.689	0.4815	0.0586
18	0.694	0.4855	0.0546
24	0.699	0.4894	0.0507
48	0.716	0.5027	0.0374

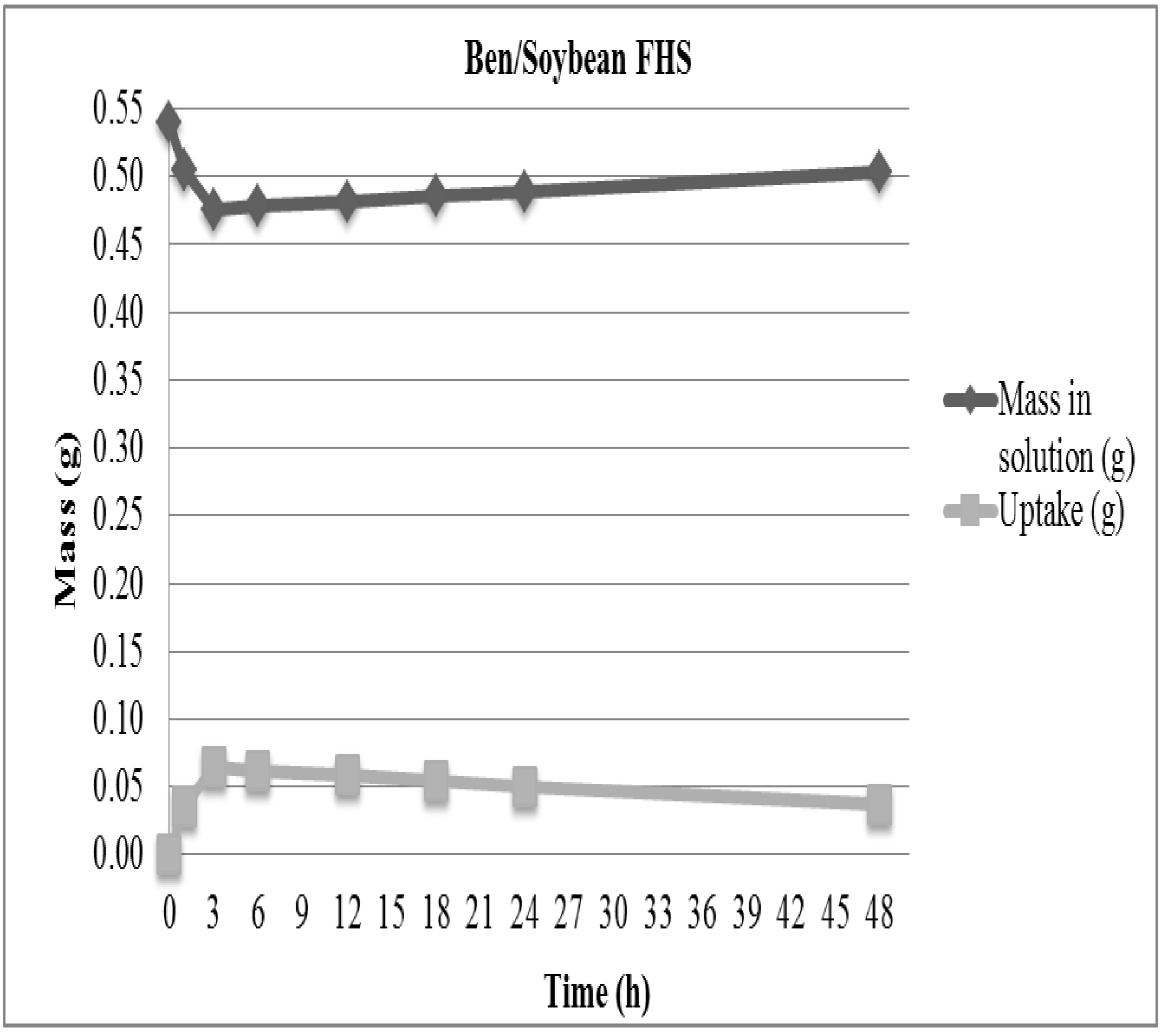


Figure 3.37. Mass uptake of FHS from soybean oil by Ben with time.

Table (3.28): The mass and mass uptake by Ben (0.9438 g) with soybean FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.716	0.5036	0.0000
1	0.416	0.2671	0.2365
3	0.223	0.1155	0.3881
6	0.226	0.1178	0.3858
12	0.231	0.1218	0.3818
18	0.235	0.1249	0.3787
24	0.238	0.1273	0.3763
48	0.254	0.1398	0.3638

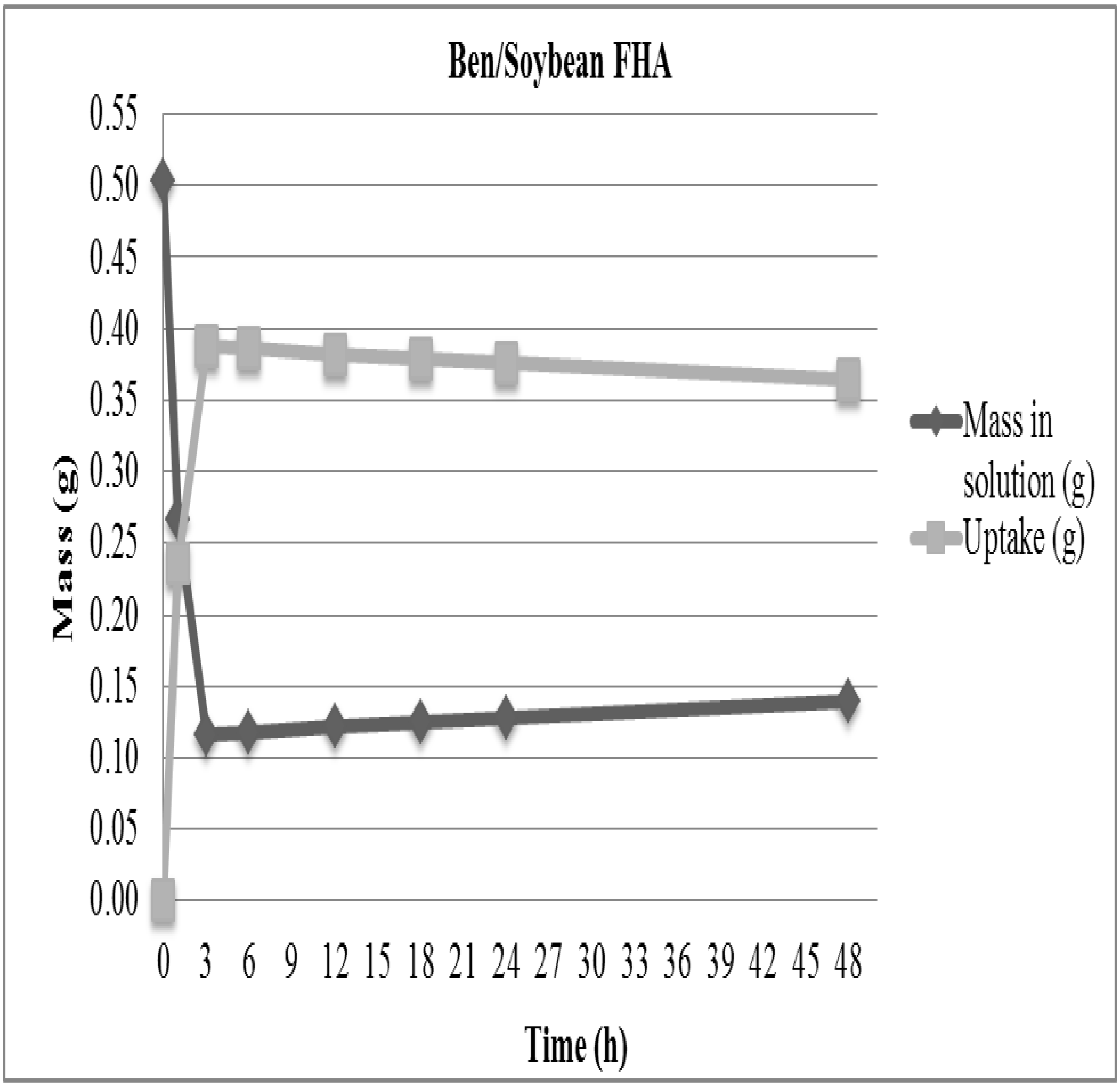


Figure 3.38. Mass uptake of FHA from soybean oil by Ben with time.

Table 3.29. The mass and mass uptake by WK (1.0871 g) with sun FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.728	0.5118	0.0000
1	0.667	0.4643	0.0475
3	0.602	0.4132	0.0986
6	0.605	0.4156	0.0962
12	0.61	0.4195	0.0923
18	0.614	0.4226	0.0892
24	0.619	0.4266	0.0852
48	0.635	0.4391	0.0727

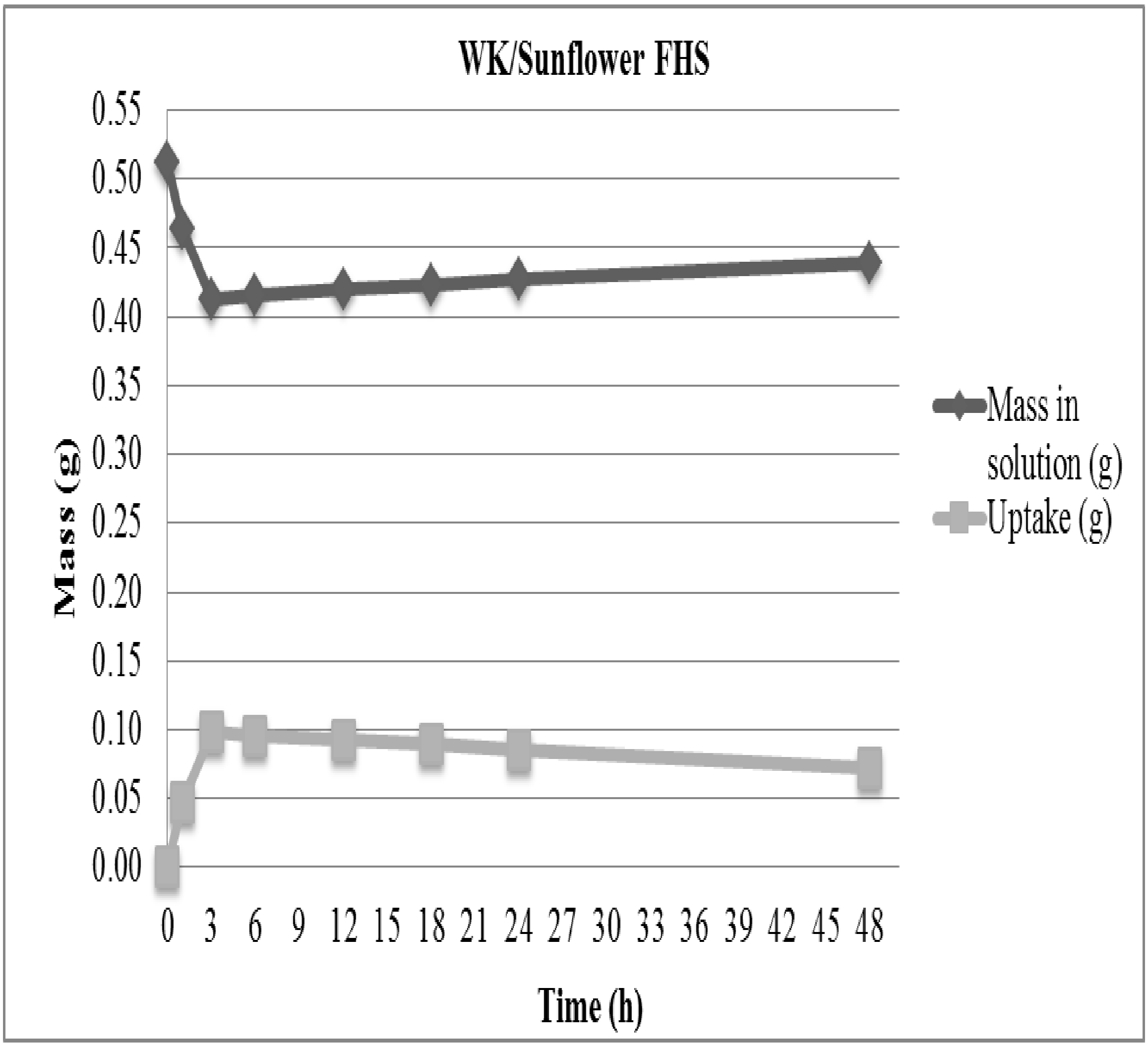


Figure 3.39. Mass uptake of FHS from sunflower oil by WK with time.

Table 3.30. The mass and mass uptake by WK (1.0563 g) with sun FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.724	0.5091	0.0000
1	0.44	0.2859	0.2232
3	0.242	0.1304	0.3787
6	0.246	0.1335	0.3756
12	0.251	0.1375	0.3716
18	0.255	0.1406	0.3685
24	0.26	0.1445	0.3646
48	0.279	0.1595	0.3496

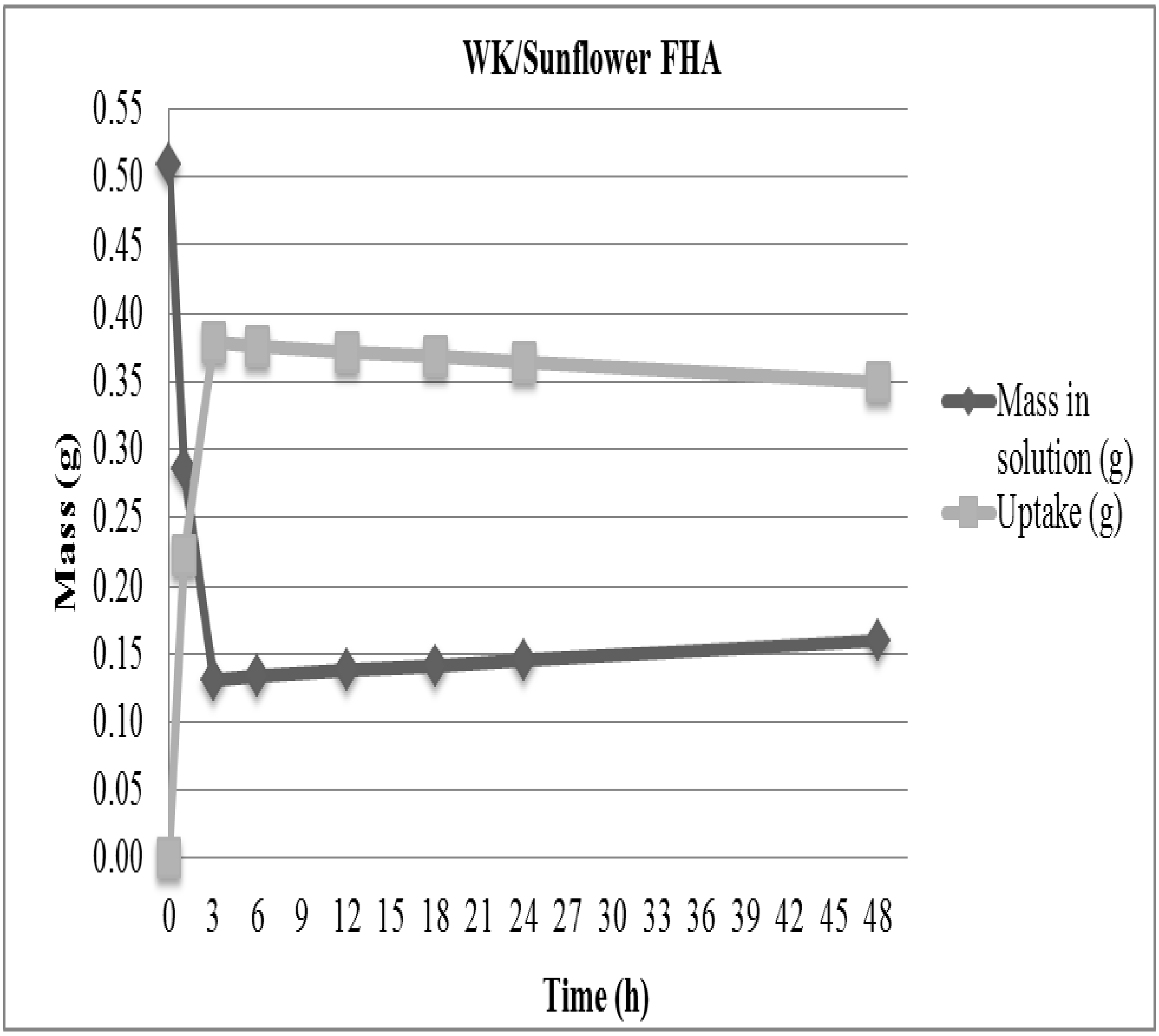


Figure 3.40. Mass uptake of FHA from sunflower oil by WK with time.

Table 3.31. The mass and mass uptake by RK (1.0564 g) with sun FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.718	0.5046	0.0000
1	0.649	0.4501	0.0545
3	0.573	0.3904	0.1142
6	0.576	0.3928	0.1118
12	0.58	0.3959	0.1087
18	0.585	0.3998	0.1048
24	0.589	0.4030	0.1016
48	0.616	0.4242	0.0804

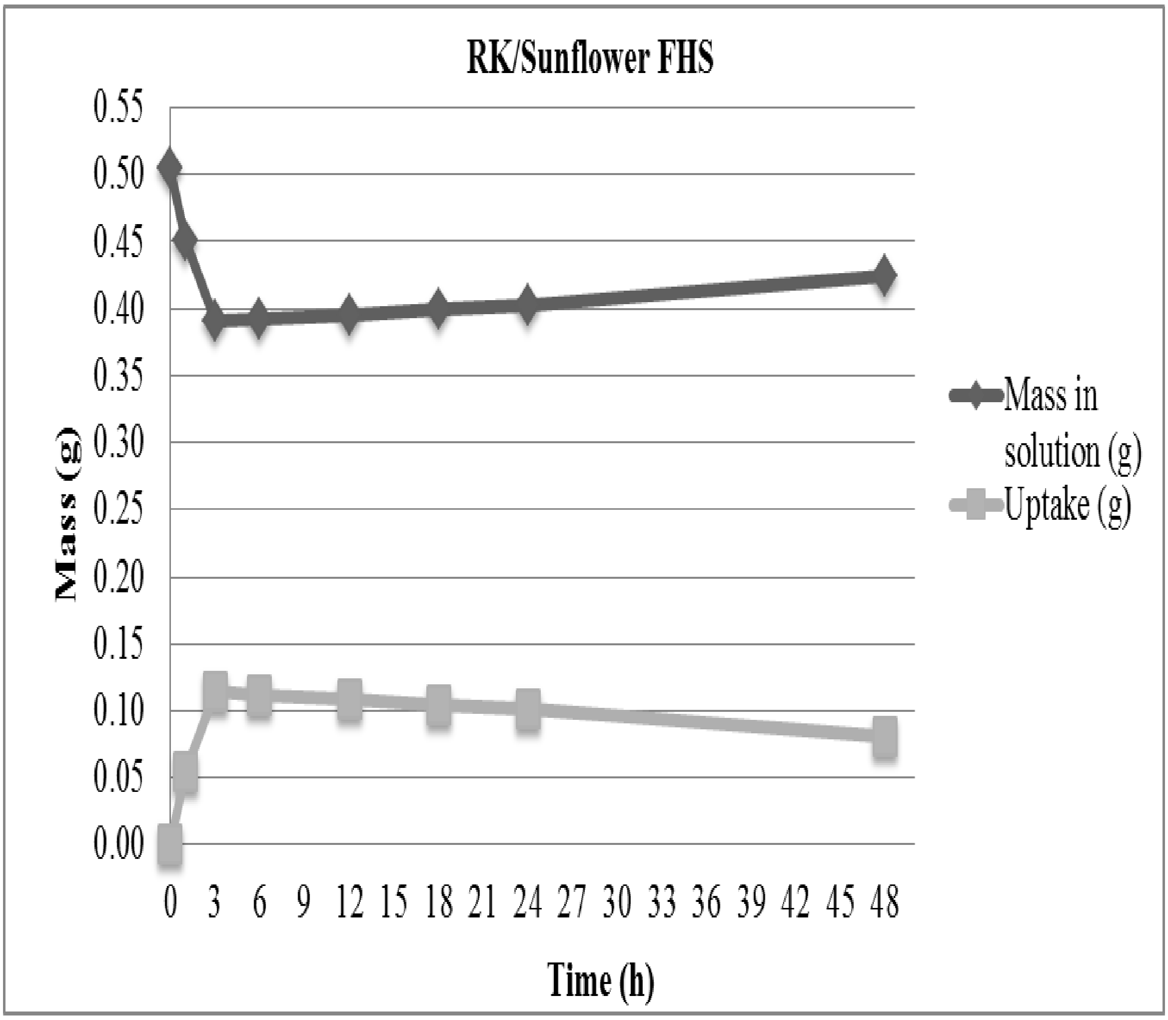


Figure 3.41. Mass uptake of FHS from sunflower oil by RK with time.

Table 3.32. The mass and mass uptake by RK (1.0569 g) with sun FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.728	0.5122	0.0000
1	0.379	0.2380	0.2742
3	0.194	0.0927	0.4195
6	0.198	0.0958	0.4164
12	0.202	0.0990	0.4132
18	0.207	0.1029	0.4093
24	0.212	0.1068	0.4054
48	0.229	0.1202	0.3920

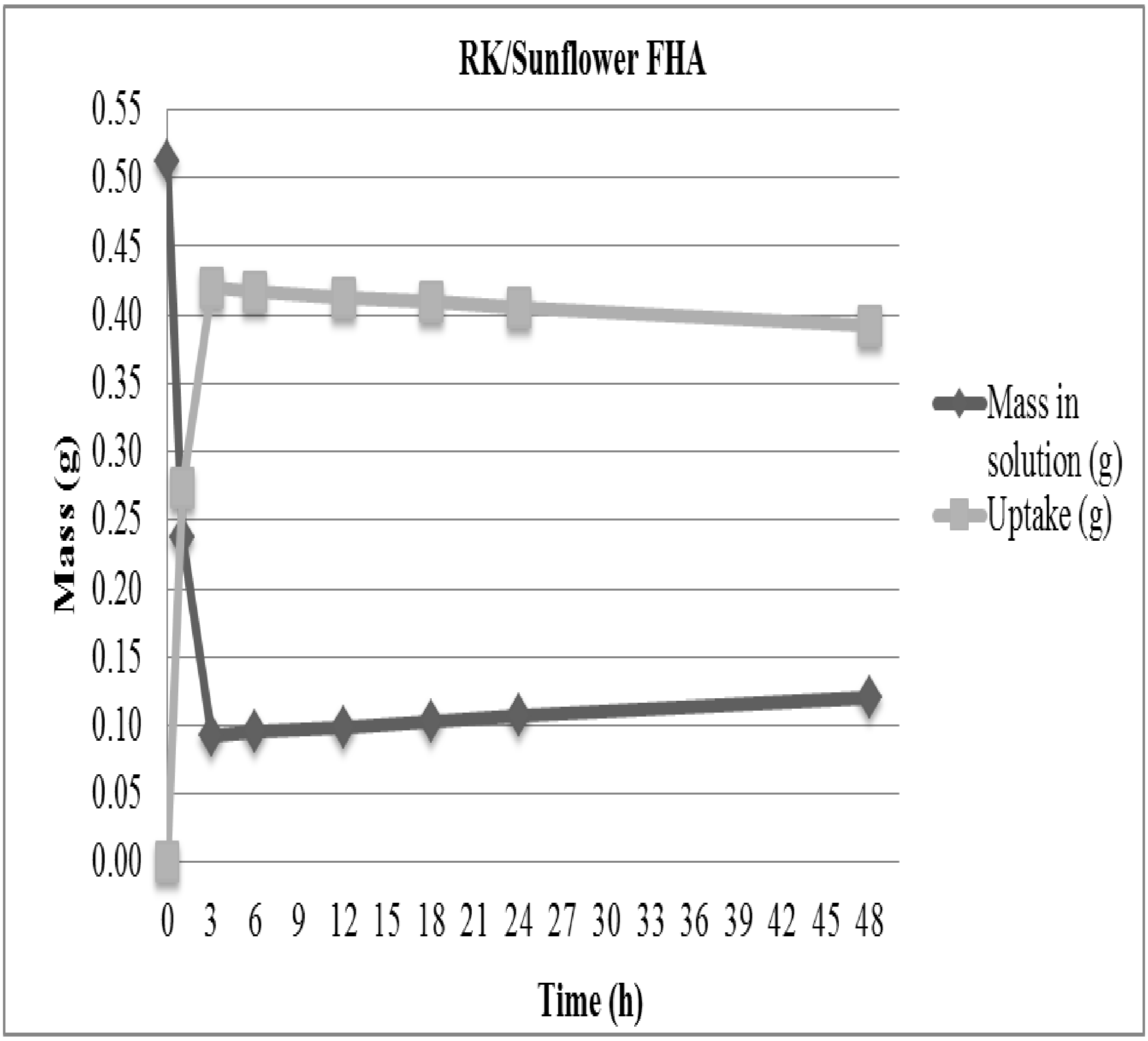


Figure 3.42. Mass uptake of FHA from sunflower oil by RK with time.

Table 3.33. The mass and mass uptake by Ben (1.0362 g) with sun FHS.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.745	0.5261	0.0000
1	0.708	0.4965	0.0296
3	0.662	0.4603	0.0658
6	0.665	0.4627	0.0634
12	0.669	0.4658	0.0603
18	0.674	0.4698	0.0563
24	0.679	0.4737	0.0524
48	0.696	0.4870	0.0391

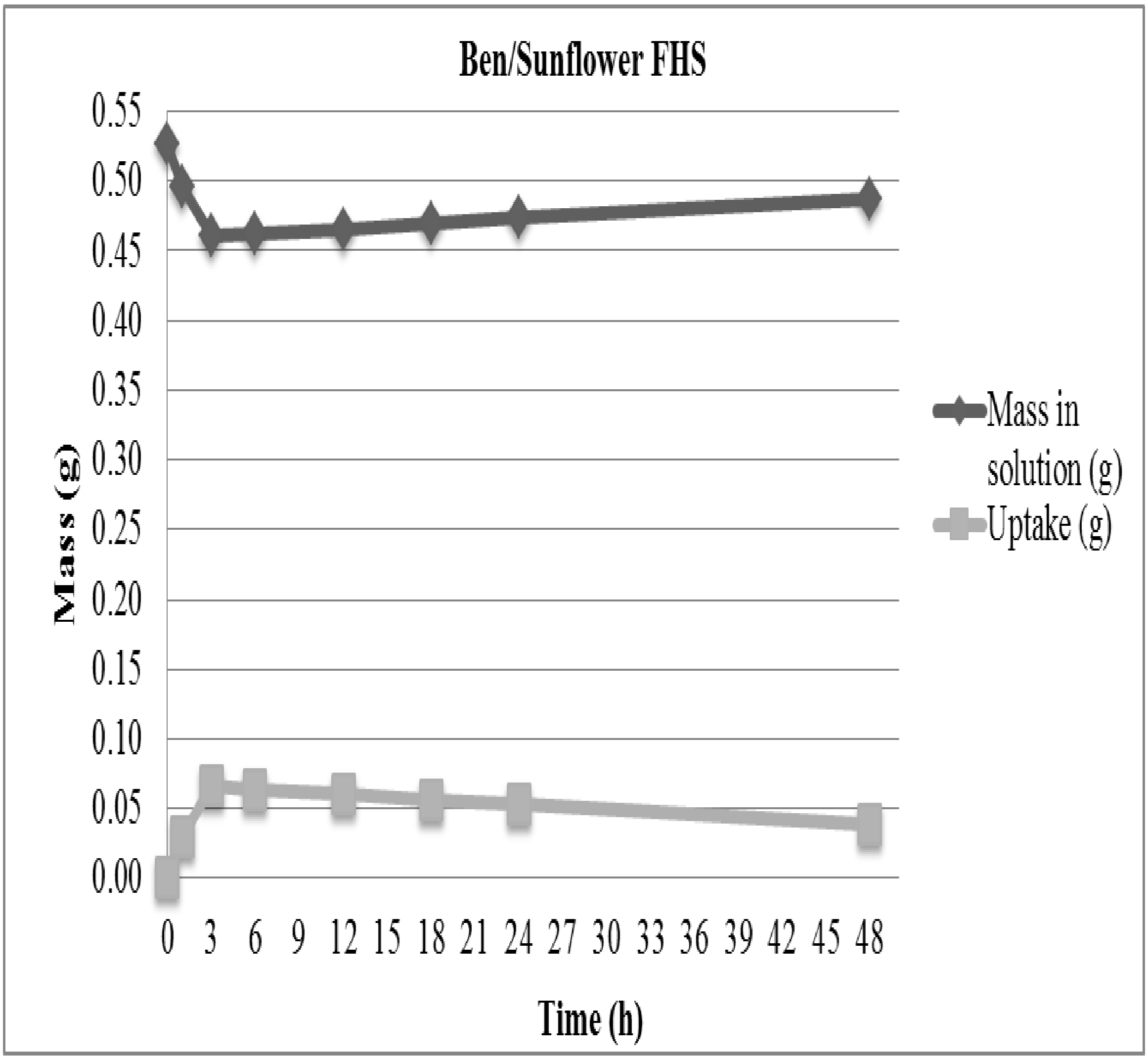


Figure 3.43. Mass uptake of FHS from sunflower oil by Ben with time.

Table 3.34. The mass and mass uptake by Ben (1.1197 g) with sun FHA.

Time (h)	Absorption	Mass in solution (g)	Uptake (g)
0	0.7550	0.5337	0.0000
1	0.3960	0.2514	0.2823
3	0.2030	0.0998	0.4339
6	0.2060	0.1021	0.4316
12	0.2100	0.1053	0.4284
18	0.2140	0.1084	0.4253
24	0.2190	0.1123	0.4214
48	0.2350	0.1249	0.4088

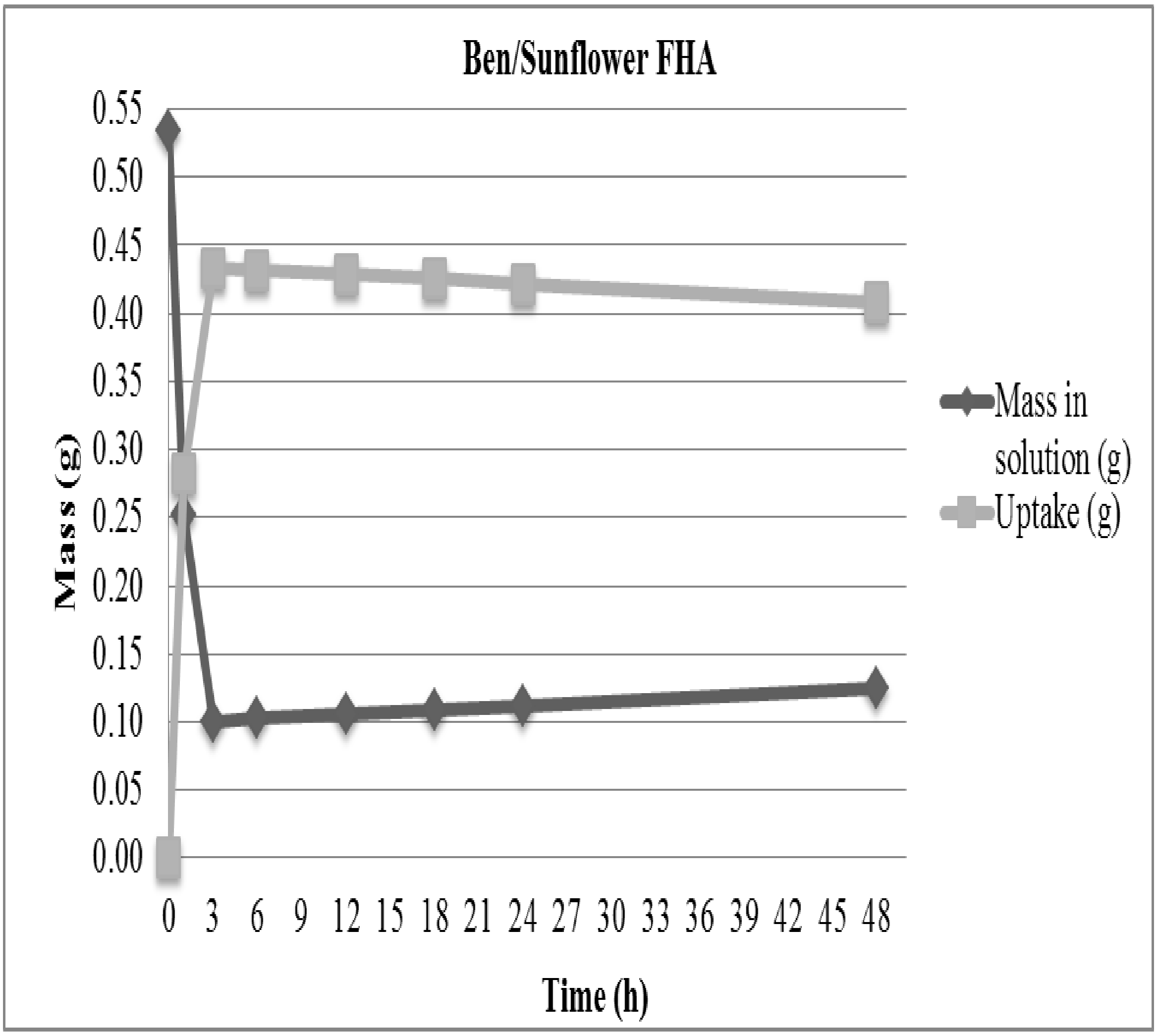


Figure 3.44. Mass uptake of FHA from sunflower oil by Ben with time.

Table 3.35. Mass uptake ratio of corn FHA/S with different types of clay.

Type of clay	WK / OH^-	WK/H^+	RK / OH^-	RK/H^+	Ben / OH^-	Ben /H^+
Mass uptake (g)	0.0999	0.3774	0.1348	0.4350	0.0650	0.4076
Mass of clay (g)	1.0538	1.0129	1.0819	1.0517	0.9326	1.0030
Uptake ratio (g/g)	0.0948	0.3726	0.1246	0.4136	0.0697	0.4064

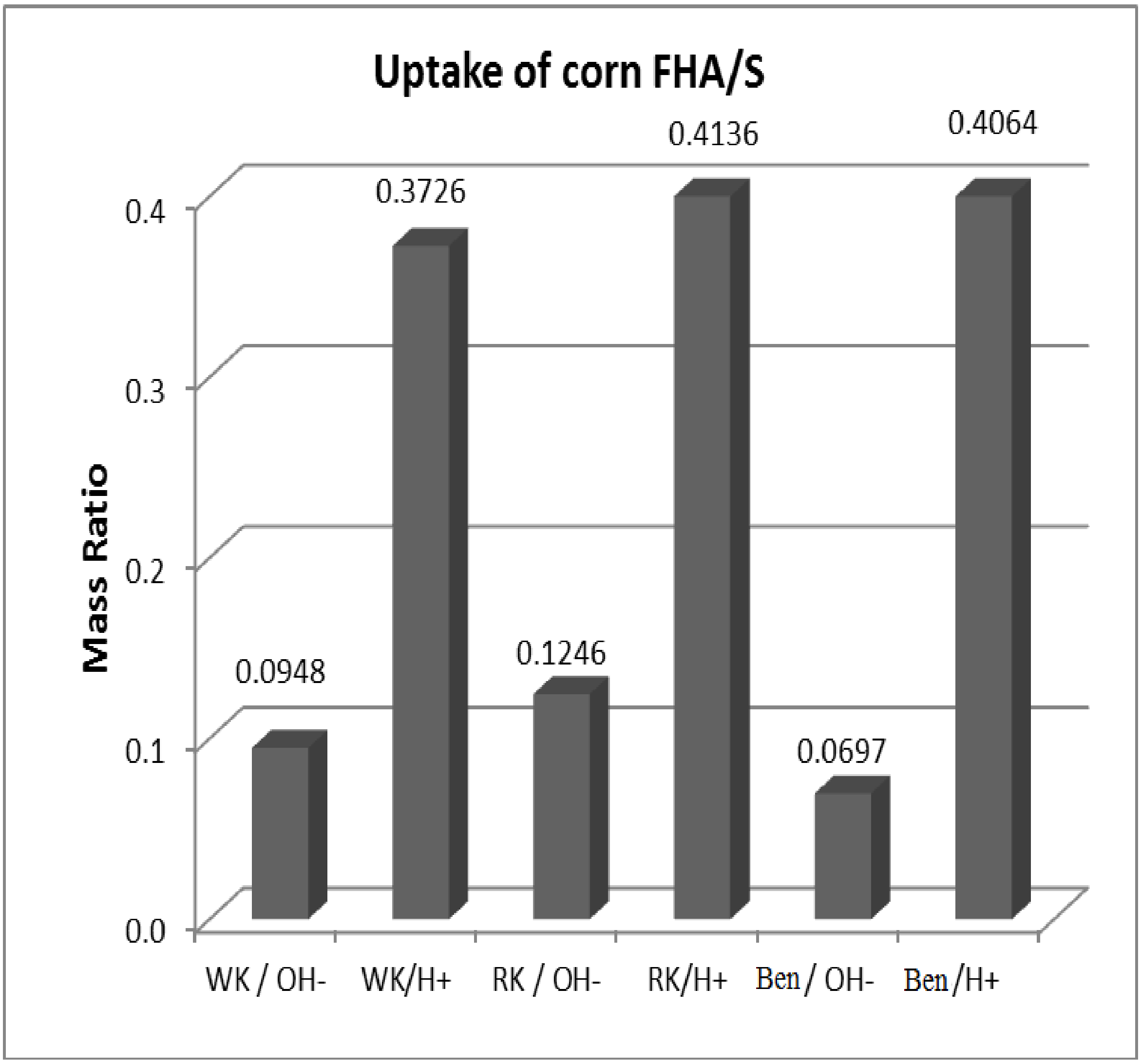


Figure 3.45. Uptake ratio of corn FHA/S with different types of clay.

Table 3.36. Uptake ratio of olive FHA/S with different types of clay.

Type of clay	WK / OH^-	WK/H^+	RK / OH^-	RK/H^+	Ben / OH^-	Ben /H^+
Mass uptake (g)	0.1523	0.3757	0.1436	0.4409	0.0731	0.4204
Mass of clay (g)	1.6289	1.0401	1.2180	1.0838	1.0766	1.0523
Uptake ratio (g/g)	0.0935	0.3612	0.1179	0.4068	0.0679	0.3995

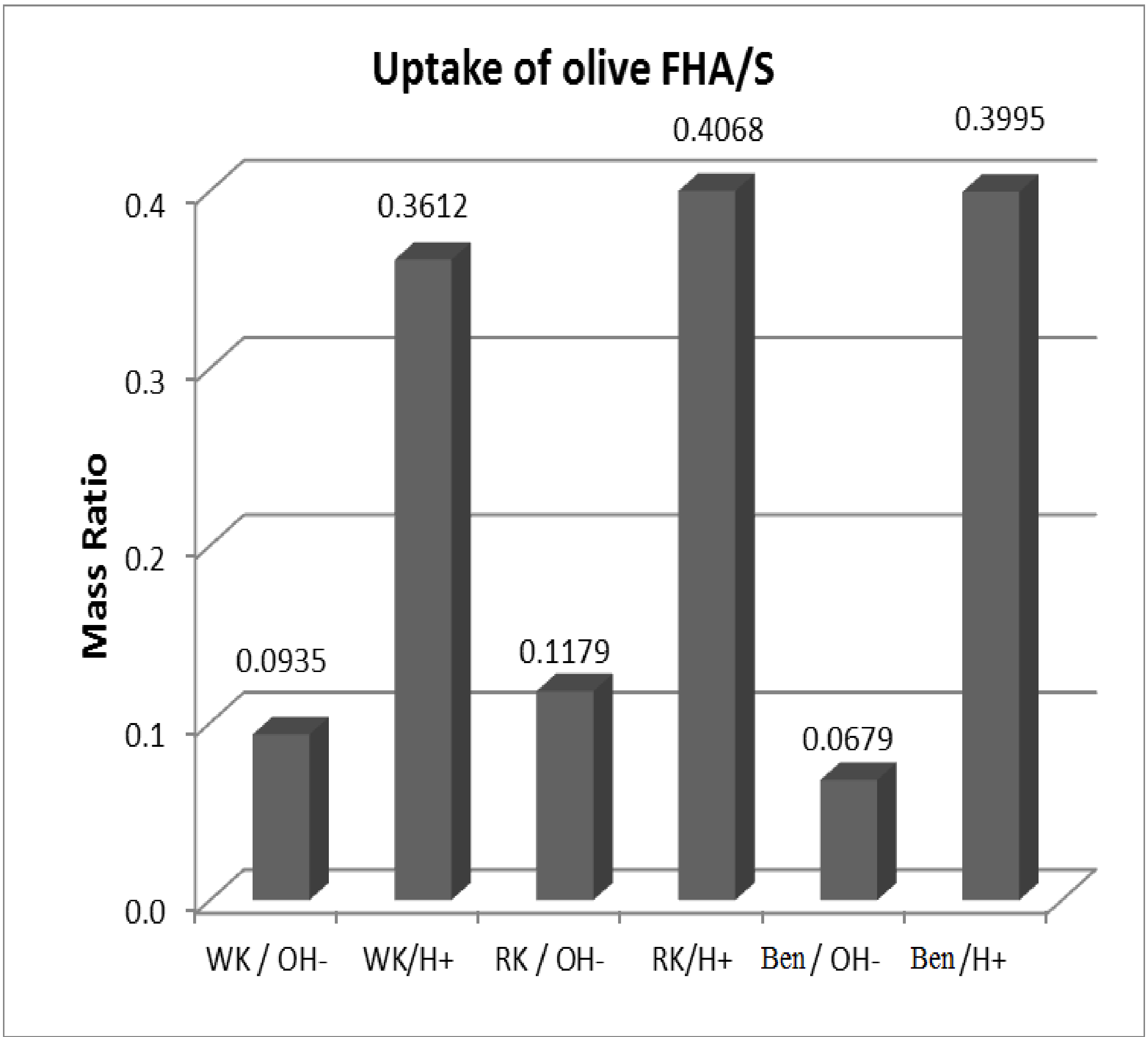


Figure 3.46. Uptake ratio of olive FHA/S with different types of clay.

Table 3.37. Uptake ratio of palm FHA/S with different types of clay.

Type of clay	WK / OH^-	WK/H^+	RK / OH^-	RK/H^+	Ben / OH^-	Ben /H^+
Mass uptake (g)	0.1051	0.4086	0.1393	0.4480	0.0790	0.4176
Mass of clay (g)	1.0813	1.0200	1.0380	1.0207	1.0025	0.9924
Uptake ratio (g/g)	0.0972	0.4006	0.1342	0.4389	0.0788	0.4208

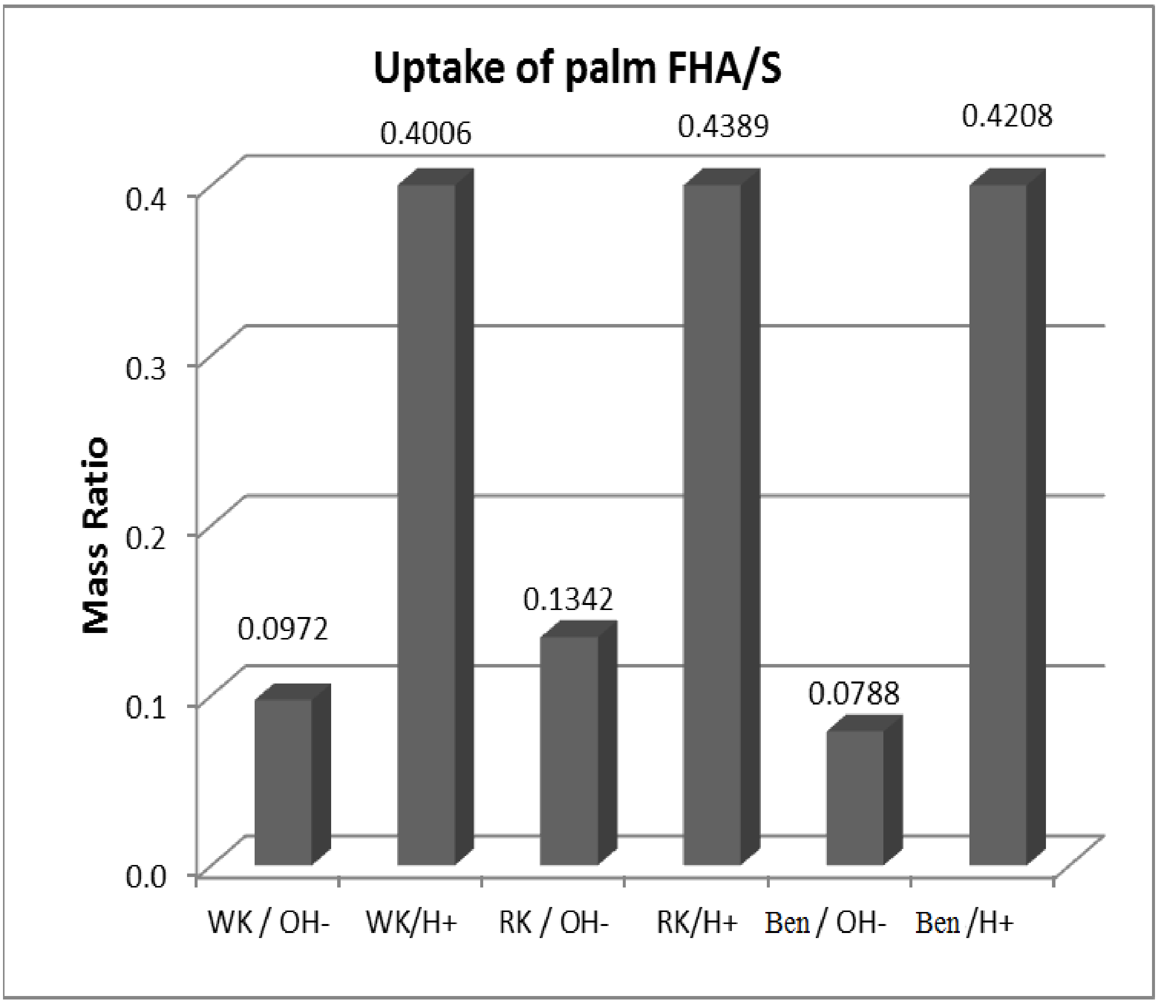


Figure 3.47. Uptake ratio of palm FHA/S with different types of clay.

Table 3.38. Uptake ratio of soybean FHA/S with different types of clay.

Type of clay	WK / OH^-	WK/H^+	RK / OH^-	RK/H^+	Ben / OH^-	Ben /H^+
Mass uptake (g)	0.1244	0.3636	0.1531	0.4294	0.0641	0.3881
Mass of clay (g)	1.3054	0.9447	1.1804	1.0183	0.8890	0.9438
Uptake ratio (g/g)	0.0953	0.3849	0.1297	0.4217	0.0721	0.4112

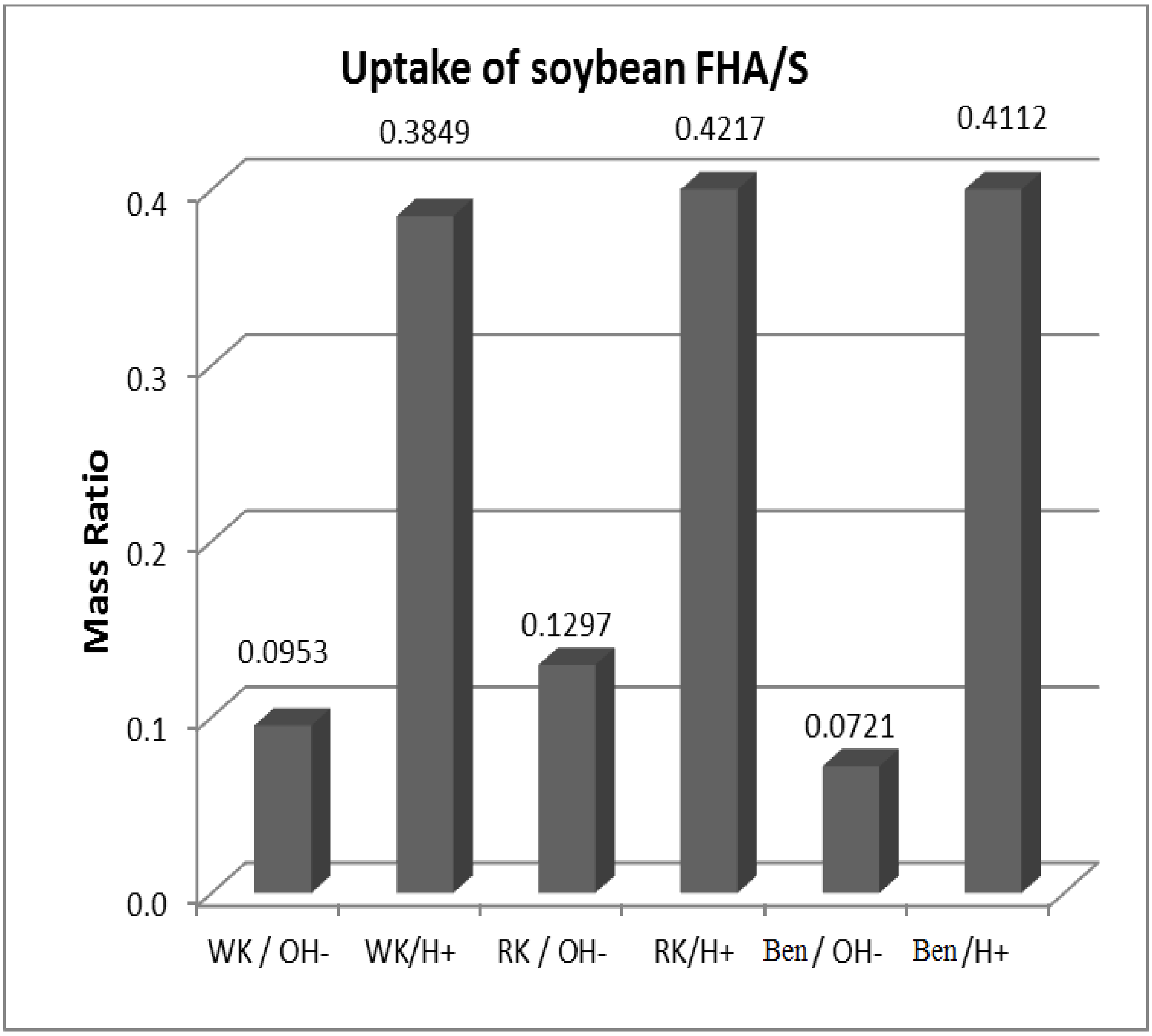


Figure 3.48. Uptake ratio of soybean FHA/S with different types of clay.

Table 3.39. Uptake ratio of sunflower FHA/S with different types of clay.

Type of clay	WK / OH^-	WK/H^+	RK / OH^-	RK/H^+	Ben / OH^-	Ben /H^+
Mass uptake (g)	0.0986	0.3787	0.1142	0.4195	0.0658	0.4339
Mass of clay (g)	1.0871	1.1458	1.0564	1.0569	1.0362	1.1197
Uptake ratio (g/g)	0.0907	0.3305	0.1081	0.3969	0.0635	0.3875

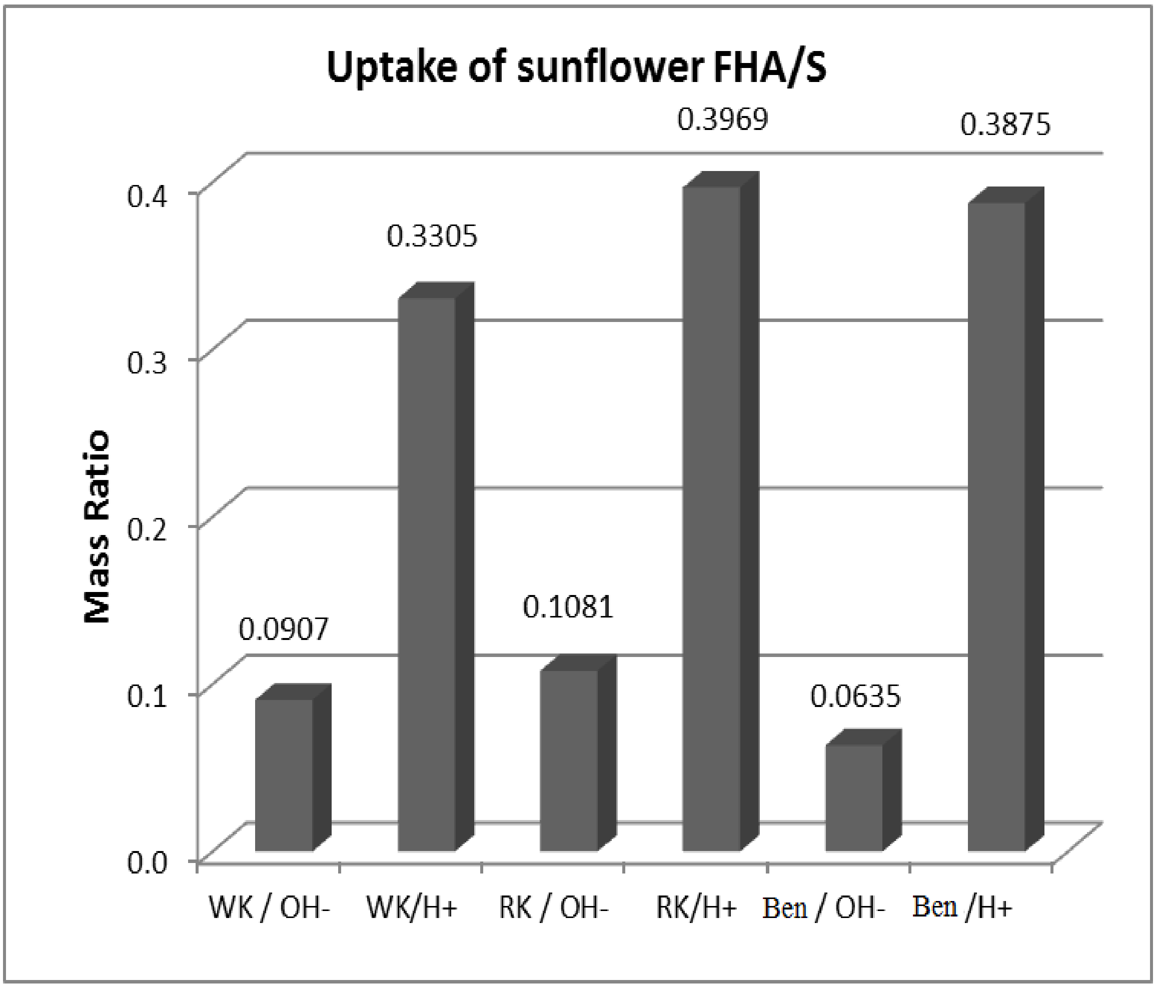


Figure 3.49. Uptake ratio of sunflower FHA/S with different types of clay.

Table 3.40. Mass uptake WK in basic solution with difirant oils.

Corn	Palm	Olive	Soybean	Sun
0.0948	0.0972	0.0935	0.0953	0.0907

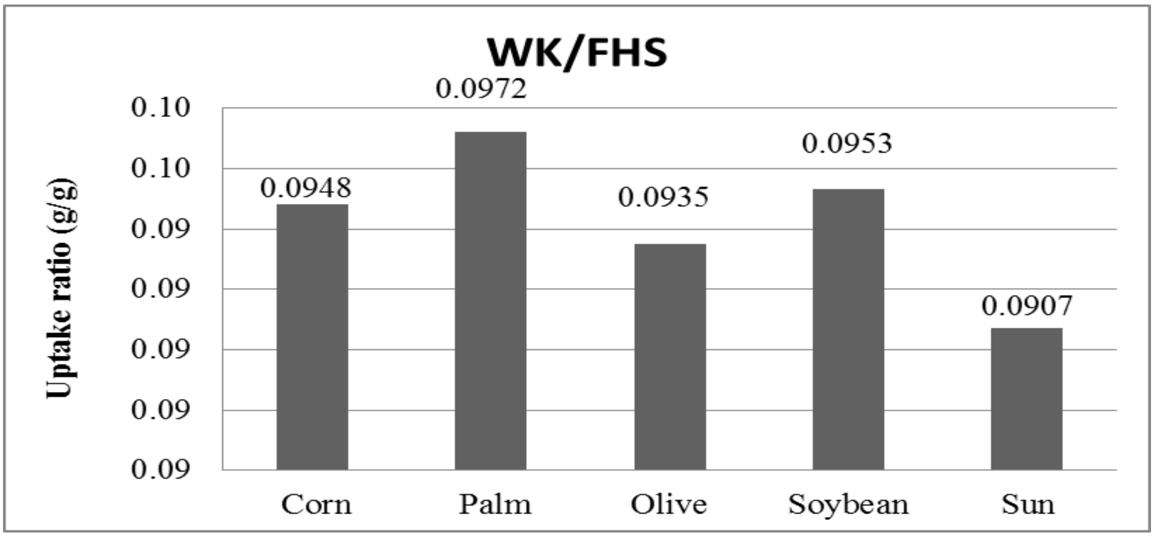


Figure 3.50. Mass uptake by WK in basic solution with different oils.

Table 3.41. Mass uptake WK in acidic solution with different oils.

Corn	Palm	Olive	Soybean	Sun
0.3726	0.4006	0.3612	0.3849	0.3305

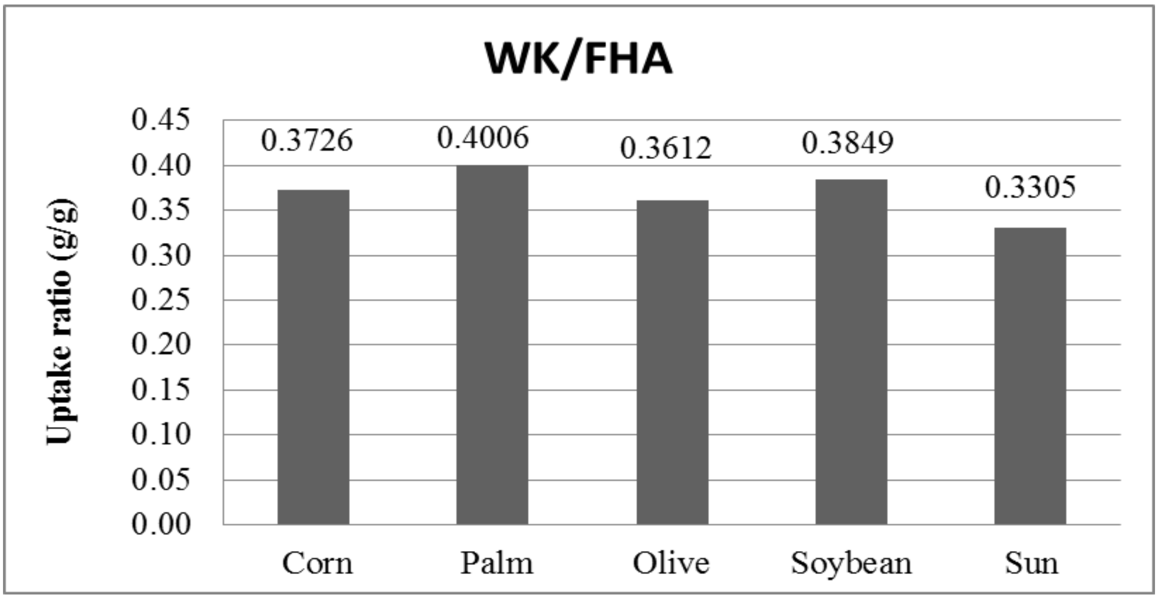


Figure 3.51. Mass uptake by WK in acidic solution with different oils.

Table 3.42. Mass uptake RK in basic solution with different oils.

Corn	Palm	Olive	Soybean	Sun
0.1246	0.1342	0.1179	0.1297	0.1081

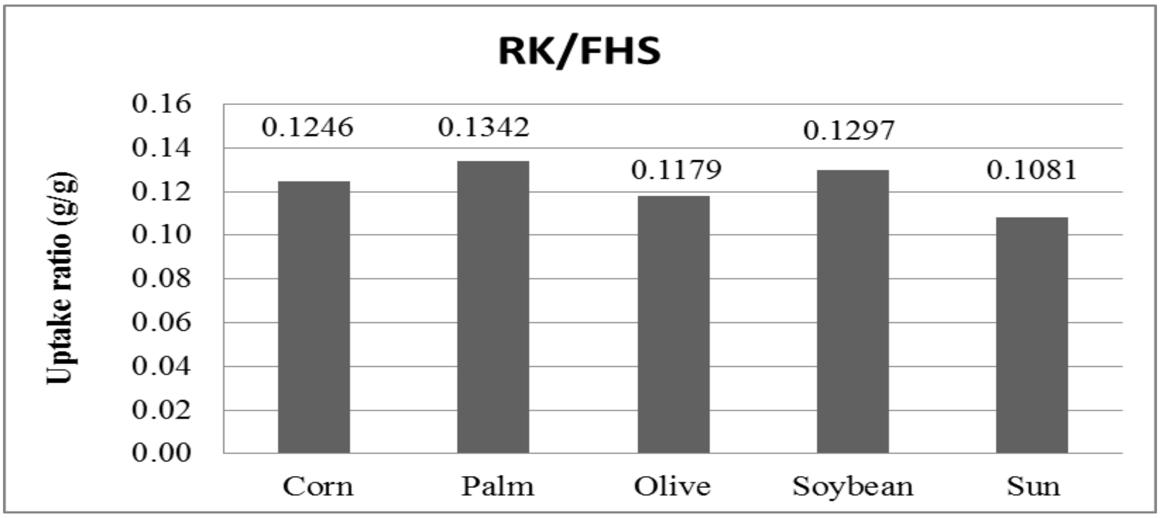


Figure 3.52. Mass uptake by RK in basic solution with different oils

Table 3.43. Mass uptake RK in acidic solution with different oils.

Corn	Palm	Olive	Soybean	Sun
0.4136	0.4389	0.4068	0.4217	0.3969

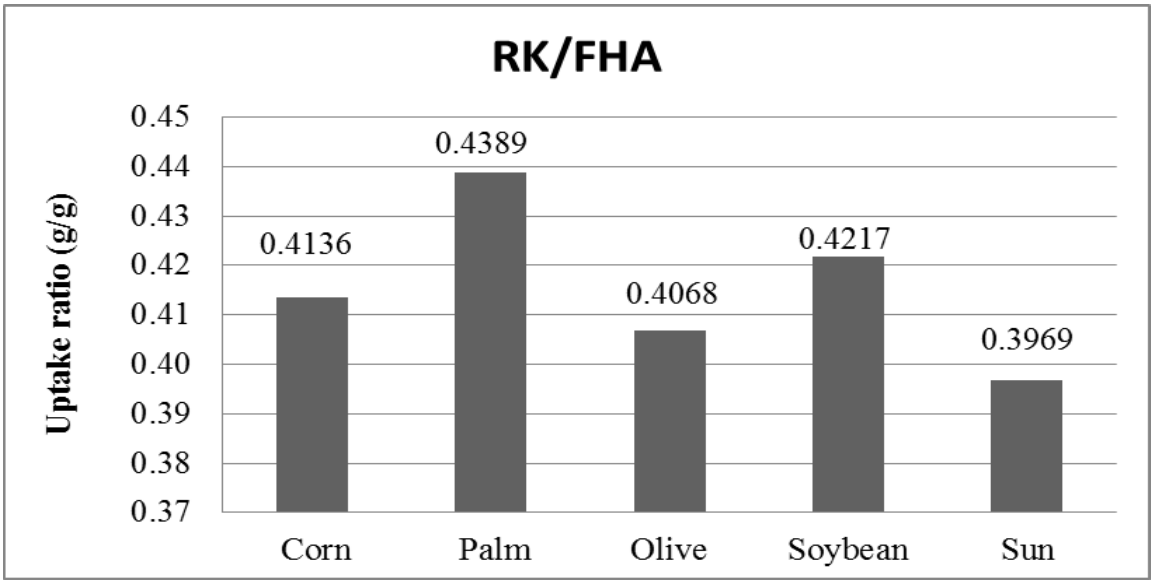


Figure 3.53. Mass uptake by RK in acidic solution with different oils

Table 3.44. Mass uptake Ben in basic solution with different oils.

Corn	Palm	Olive	Soybean	Sun
0.0697	0.0788	0.0679	0.0721	0.0635

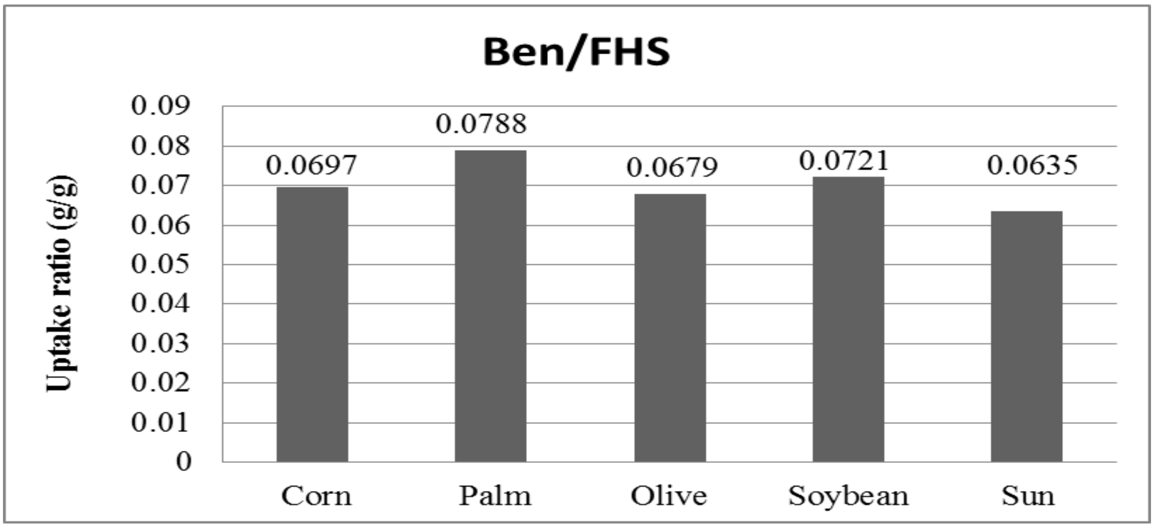


Figure 3.54. Mass uptake by Ben in basic solution with different oils

Table 3.45. Mass uptake Ben in acidic solution with different oils.

Corn	Palm	Olive	Soybean	Sun
0.4064	0.4208	0.3995	0.4112	0.3875

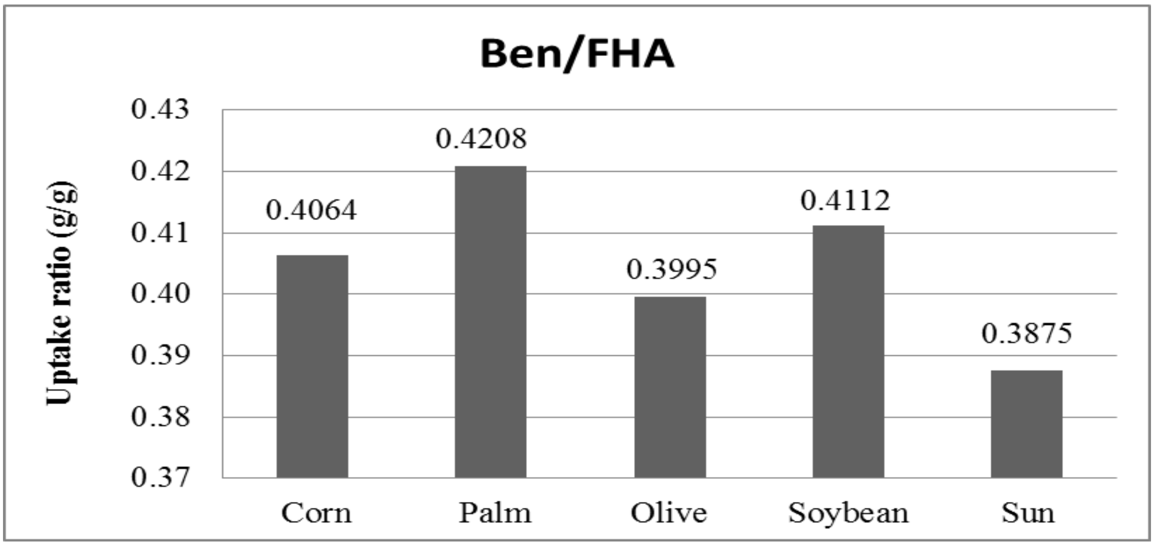


Figure 3.55. Mass uptake by Ben in acidic solution with different oils

Conclusions

1. FHAs were successfully prepared from several vegetable oils by three methods including carboxylic, methyl/ethyl ester and triacylglyceride.

2. All FHA were used to modified three clays namely, white kaolin, red kaolin and bentonite. The modifications were carried out in acidic and basic medium.

3. The mass uptake were observed to be better in acidic than in basic medium.

4. The maximum mass uptake was obtained by using red kaolin modified by palm FHA in acidic medium.

5. The mass spectroscopy results showed that the synthesis of FHA.

Future work

1. Study how to prepare FHA by chemical catalysts.

2. Study the complexes that FHA can make.

3. Make isothermal and kinetically studies for the modified clay.

4. Identify the modified clay by more advanced and precise Instruments such like TGA, elemental analysis, advanced XRD, and single crystal X-ray.

5. Modify the red kaolin to remove its impurities, and make it brighter and whiter.

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تعديل الطين الأردني باستخدام الأحماض الدهنية الهيدروكسامية و المحضرة من عدة زيوت نباتية

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الملخص

تم دراسة وتحضير و تشخيص الاحماض الدهنية الهيدروكسامية (FHA) و المحضرة من زيوت نباتية مختلفة هي: زيت الذرة, زيت النخيل, زيت فول الصويا, و زيت دوار الشمس, و زيت الزيتون. لقد تم تحضير الأحماض الدهنية الهيدروكسمية (FHA) من الزيوت النباتية بإستخدام ثلاثة طرق وهي: i) تحضيرها من الحوامض الدهنية الكاربوكسيلية, ii) تحضيرها من الحوامض الدهنية بصيغتها الاستيرية,iii) وبشكل مباشر من جليسيرات ثلاثية الأسيل. تم تشخيص جميع الأحماض المحضرة باستخدام مطيافية الأشعة تحت الحمراء و الكتلة, و التي اثبتت التراكيب الجزئية لهذه الحوامض. تم استخدام هذه الاحماض الدهنية (FHA) بتحوير و تحسين الأداء لثلاثة أنواع من الأطيان هي الكاولين الأبيض, و الأحمر, و البنتونايت. تم تشخيص الأطياف المحورة والمعدلة باستخدام المجهر الماسح الإلكتروني و تقنية حيود الأشعة السينية و مطيافية الأشعة تحت الحمراء. أثبتت نتائج التشخيص ان التحوير قد تم بالفعل. تم اجراء تجارب عملية لاجاد الكتل المحملة من الحوامض الدهنية الهيدروكسامية على سطوح هذه الأطيان وفي وسطين هما الحامضي والقاعدي. أثبتت التجارب بأن الكتلة المحملة على سطح الكاولين الأحمر من الحمض الدهني المحضر من زيت النخيل كان الأكثر تحميلا مقارنة بالطينين الاخريين و بقية الزيوت النباتية . أثبتت جميع التجارب بأن تحميل الحوامض الدهنية المحضرة من الزيوت النباتية و المحتوية على ذرات اكسجين و نيتروجين كفاءتها لتحوير و تحسين اداء الامتزاز (الكتلة المحملة) لهذه الأطيان.